MULTIELEMENT ATOMIC FLUORESCENCE FLAME SPECTROMETRY: EVALUATION OF A PULSED EIMAC CONTINUUM SOURCE AND CHARACTERIZATION OF BACKGROUND MOLECULAR FLUORESCENCE

BY

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This work is dedicated to my parents, Mr. William B. Fowler and Mrs. Josephine H. Fowler, who have inspired me to some degree by filial instruction but far more profoundly by living example, and whose moral and financial support were vital to my success as a graduate student.

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	iii
ABSTRACT	v
CHAPTER I. GENERAL INTRODUCTION AND BACKGROUND	1
CHAPTER II. EVALUATION OF A PULSED EIMAC SOURCE	9
CHAPTER III. THE SPECTRUM OF THE FLUORESCENCE BACKGROUND	28
CHAPTER IV. FURTHER CHARACTERIZATION OF THE FLUORESCENCE OF PO	58
CHAPTER V. CONCLUSIONS AND DIRECTIONS FOR FURTHER RESEARCH	77
REFERENCES	80
BIOGRAPHICAL SKETCH	84

Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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An Eimac xenon arc continuum source operated in the pulsed mode has been evaluated for potential use as a source of excitation in atomic fluorescence spectrometry. Limits of detection, precision data, and analytical curves were determined for several elements in the argon separated air-acetylene flame, and the limits of detection are compared to those obtained with a similar lamp operated in the cw mode. Little or no improvement is evident from this comparison; the lamp was found to be relatively unstable in the pulsed mode, requiring the use of a rather large residual dc current in conjunction with a relatively low-amplitude power pulse in order to sustain the arc. Moreover, the pulsed source yielded a large background signal due to scattering of incident source radiation in the flame, and the background fluorescence spectrum contained numerous

large peaks due to fluorescence of molecular species in the flame and/or to prominent peaks in the spectral distribution of the pulsed lamp output, transferred to the signal detector via scatter.

The numerous peaks observed in the fluorescence background spectra of the pulsed source studies have been evaluated separately. An attempt was made to identify each of the observed peaks and bands, with the result that molecular fluorescence bands were measured and assigned to PO, NH, CN, and OH. In addition, peaks resulting from the grating second order of PO fluorescence bands were observed. The spectral distribution of the source radiation was measured in both the pulsed and cw modes, but none of the spectral irregularities detected in the flame fluorescence background spectra were found to correspond to scatter peaks in the source spectral output. Background fluorescence spectra were recorded under three different analytically useful sets of flame conditions (fuel-lean, stoichiometric fuel-rich), and spectra obtained in both the pulsed and cw modes are compared. A commercially available filter designed to remove PH_3 from acetylene was evaluated with respect to its ability to reduce the fluorescence intensity of PO, a species formed in the flame from PH_3, present in the acetylene as an impurity. A general assessment of molecular fluorescence in flames as a source of interference in atomic fluorescence spectrometry is presented.

Because the flame fluorescence of PO was discovered to be particularly intense and widely distributed in the spectrum, it has been further characterized in a separate study. PO fluorescence signals generated by phosphate solutions were compared to those produced only by the PH_3 impurity in the acetylene. The fluorescence and emission intensities of PO were compared in various flames, and a silicon intensified target (SIT) tube in conjunction with an optical multichannel analyzer (OMA) was evaluated for potential application to the study of molecular fluorescence in flames. The possibility of utilization of PO fluorescence for the analysis of phosphorus was investigated; the analytical precision and limit of detection for phosphorus determinations were estimated from signals produced by standard solutions of phosphoric acid nebulized into various flames.

CHAPTER I

GENERAL INTRODUCTION AND BACKGROUND

The phenomenon of atomic fluorescence was first observed in sodium vapor by Wood in 1904 (1) but was not seen in flames until 1924, when Nichols and Howes (2) detected the fluorescence of several elements in a Bunsen burner flame. Atomic fluorescence subsequently attracted little interest until 1962, when Alkemade (3) suggested its use as an analytical technique. In 1964, Winefordner and Vickers (4) published the first paper characterizing the method with regard to theoretical principles and experimental requirements, and since then, numerous studies embracing virtually every aspect of atomic fluorescence spectrometry have been published.

For the analysis of elements which are difficult to excite in emission, atomic fluorescence spectrometry maintains several theoretical and practical advantages, with regard to sensitivity, over the more conventional methods of atomic absorption and atomic emission spectrometry (4-7). The analytical sensitivity of atomic absorption spectrometry is limited by the ability of the signal detection system to respond measurably to small changes in light level at the photocathode caused by the absorption process within

the sample cell. An increase in source intensity at the wavelength of the spectral line may improve the detection limits for the technique, provided the RMS noise level on the observed signal is increased by a smaller factor; however, stable, narrow-line, unreversed sources are required, unless a very high-quality, narrow spectral bandpass monochromator is used. To date, only the moderately intense hollow cathode discharge tubes meet these requirements to an extent sufficient to allow atomic absorption spectrometry to compete with atomic fluorescence spectrometry in terms of detection limits for trace elemental analysis. Attempts (other than pulsing of the source) to boost the output intensity of these sources without seriously degrading their most desirable characteristics and/or introducing other undesirable features have largely failed (8,9).

On the other hand, source and monochromator requirements in atomic fluorescence spectrometry are considerably less stringent; the monochromator "sees" only fluorescence, not the excitation source radiation which produces it. Accordingly, very intense, broad-line sources may be used to advantage in this technique, because the intensity of fluorescence is proportional to the source irradiance at the wavelength of the excitation line. A variety of excitation sources have been shown to be adaptable to atomic fluorescence spectrometry (10,11), and several of these have manifested considerable promise for augmentation of their output intensities (12,13). Furthermore, it is

possible to employ a single continuum source for all elements, while utilizing at the same time a relatively inexpensive, low-dispersion monochromator in the signal detection system. In practical applications of atomic fluorescence spectrometry, improvements in signal-to-noise ratio to be obtained from increases in excitation source irradiance are eventually limited only by those types of noise whose magnitudes are directly proportional to the first power of the source irradiance.

Atomic fluorescence spectrometry has the advantage over atomic emission spectrometry that the analytical signal is directly proportional to the concentration of atoms boosted to the excited state via radiational excitation rather than to the concentration of atoms in the excited state due to thermal excitation. Thus, the atomic fluorescence signal should be less dependent upon flame temperature, and the technique should be more applicable to elements which are difficult to excite by thermal means.

Despite its potential advantages, atomic fluorescence spectrometry suffers from a number of important fundamental limitations. Of the three flame techniques for multi-element analysis, atomic fluorescence spectrometry is most affected by the quenching abilities of certain flame gas constituents (5). Quenching of excited atoms is caused by non-radiative de-activation of the excited state resulting from collisions with molecules during the lifetime

of the excited state. Moreover, because the measurement of a very small quantity of light is involved, any extraneous source of radiation at the wavelength of interest which is passing light into the monochromator (within the proper light-gathering solid angle) along with the analyte fluorescence may constitute a serious interference and even if corrected for may still impose enough noise upon the signal to limit the analytical sensitivity of the system. Examples of possible extraneous signal sources include scattering of source radiation by molecules and atoms, by solid particles, and by unevaporated solvent droplets in the flame, flame background emission (both atomic and molecular), and spectral interferences from overlapping fluorescence lines (atomic) and bands (molecular). Other limitations affecting the measurement of atomic fluorescence signal have been described (14).

Because the potential advantages to be derived from increasing the intensity of available excitation sources in atomic fluorescence spectrometry have long been recognized, numerous researchers have attempted to increase the peak outputs of sources conventionally operated in the cw mode by pulsing these sources with an intermittent duty factor at high peak input powers, while maintaining the average input power at the usual level (15). By gating the signal detection system to coincide with the excitation source output pulse, the detector can be made to "observe"

a much higher signal level for a given analyte concentration than is possible with the same source operated in the cw mode. The signal-to-noise ratio improvement sought in these studies derives from the fact that the fluorescence signal is proportional to the peak source intensity (and is therefore larger than that obtained in the cw mode), while the background signal, and therefore the background noise, are limited by the "on" time of the gated detector (and are therefore smaller than the background signal and noise obtained in the cw mode) (16). Limitations experienced in the practical application of these techniques to atomic fluorescence spectrometry have been generally associated with the difficulty or expense of implementation and with the propensity for introduction into the system of new or special sources of noise (17).

For the analysis of a multielement mixture by atomic fluorescence spectrometry, a potentially attractive alternative to the use of conventional line sources of excitation is the possibility of simultaneous excitation of many elements with a single continuum source. Available continuum sources offer good stability, long useful life, and simplicity of operation as compared to many line sources, particularly electrodeless discharge lamps and hollow cathode discharge lamps. However, several studies (17-19) have indicated that an important limitation associated with the application of continuum sources to analytical atomic

fluorescence spectrometry is the low output intensity over atomic spectral lines, especially in the low UV (180-260 nm). As a result, limits of detection for elements with resonance lines in the low UV are typically one or two orders of magnitude worse than those obtainable with line sources. Interference from source light scattered in the flame, although considerably greater (worse) when a continuum source is used, owing to the dependence of the scatter signal in this case upon the square of the spectral bandpass of the monochromator, can be minimized by proper choice of flame and flame conditions and can be compensated for by wavelength scanning in the vicinity of the fluorescence line (18).

An evaluation of a pulsed Eimac source of excitation for use in atomic fluorescence spectrometry is presented in Chapter II. Limits of detection, analytical curves, and precision data are reported for several elements, and the detection limits are compared with those obtained in a previous study (18) utilizing an Eimac lamp operated in the cw mode. Signal processing was accomplished with the photon-counting system of Reference 18.

Chapter III consists of a separate evaluation of the fluorescence background observed during the study of the pulsed Eimac source, with special regard to the numerous spectral irregularities believed to have resulted from scatter and/or molecular fluorescence, neither of which have

been reported previously in significant quantities under the particular set of experimental conditions applied to these studies. An attempt was made to identify each of the observed peaks and bands. Spectra were recorded under three different analytically useful sets of flame conditions in the flame used for the pulsed Eimac study (argon sheathed air-acetylene flame). Results obtained with the Eimac lamp operated in the pulsed and cw modes, respectively, are compared, and the spectral distribution of the lamp radiation was measured for both modes of operation. A commercially available filter designed to remove phosphine (PH_3) from acetylene (20) was evaluated in terms of its ability to reduce the fluorescence intensity of phosphorus monoxide (PO), a species formed in the flame from PH_3, present in the acetylene as an impurity.

Because the fluorescence of PO was discovered to be the most intense spectral feature in the observed background fluorescence spectra, and because molecular fluorescence in flames has been largely untreated in the literature, it was decided to characterize further the molecular fluorescence of PO. This study is described in Chapter IV of this dissertation. Signals produced by phosphate solutions were compared to signals generated only by the PH_3 impurity in the acetylene. Fluorescence and emission intensities are compared in various flames, and a silicon intensified target (SIT) tube in combination with an

optical multichannel analyzer (OMA) is evaluated for potential application to the study of molecular fluorescence. In order to investigate the potential utility of PO fluorescence for the analysis of phosphorus, the analytical precision and limit of detection for phosphorus determintions have been obtained for solutions of phosphoric acid nebulized into various flames.

The final chapter of this work contains a brief summary and conclusion, along with a few statements about possibilities for future research in these areas.

CHAPTER II

EVALUATION OF A PULSED EIMAC SOURCE

The useful photon flux reaching the atomic vapor from a continuum excitation source can be increased by increasing the input power to the source, by improving the efficiency of light gathering of the source optics, and/or by pulsing the source while synchronously gating the signal detection system. Unfortunately, there exists at present only limited room for improvement in signal-to-noise ratio to be achieved by use of (non-laser) sources with high input powers, because the output stability of many available sources deteriorates rapidly with an increase in operating current. Moreover, lamp life is generally significantly reduced, and operational difficulties may be encountered. The light-gathering efficiency of the source optics, often severely limited by the geometry of the lamp itself, seems also to have reached a practical limit for currently available sources with the design of the Eimac lamp. Therefore, pulsing of an Eimac continuum source (while synchronously gating the detector) presently appears to offer the greatest potential for increasing the usable exciting flux at the atomic vapor.

A likely fringe benefit expected to result from the pulsing of continuum sources is enhanced radiant output in

the UV (21). Such enhancement depends upon the ability of the input power pulse to increase significantly the color temperature of the source during the lifetime of the pulse.

Evaluation of a pulsed linear flash lamp continuum source for application to atomic fluorescence spectrometry was performed by Johnson, Plankey, and Winefordner (17); however, their work was considerably hampered by experimental difficulties. The high voltage pulses needed to start the xenon arc flashtube generated a great deal of RF interference, and the observed noise level was strongly dependent upon the orientation of the output cables from the pulsed power supply. Furthermore, the radiative efficiency of the long capillary flashtube, i.e., the light-gathering efficiency of the optical system, was relatively low. Their results indicated that the detection limits with the flash lamp source were approximately an order of magnitude worse than those obtained with the 150 W Eimac xenon arc lamp operated in the cw mode.

The work described here attempts to circumvent these experimental limitations through operation of an Eimac continuum source in the pulsed mode with the pulse superimposed upon a constant dc level. Efficiency of radiative transfer from source to flame is very high with this source, and it can be pulsed without the use of a high voltage pulse to initiate the discharge if a residual dc current is permitted to flow through it between pulses. A stoichiometric argon separated air-acetylene flame was used for all elements

studied in order to facilitate comparison of results with those of other atomic fluorescence studies utilizing the Eimac lamp and other sources operated in the cw mode (17-19, 22). Other experimental parameters, such as the monochromator slit width and the observation height in the flame, were also chosen with this purpose in view.

Experimental

Apparatus (see Table I). A block diagram of the system used in the present study is shown in Figure 1. Light from a pulsed Eimac xenon arc continuum source was focused by a single lens of 2 in focal length into the center of an argon separated air-acetylene flame at a fixed height above the burner top, and then reflected back through the flame with a 140 mm diameter, 62 mm focal length spherical mirror which was coated for enhanced reflection in the UV. A lens matching the f/5.3 aperture of the monochromator was positioned within the black cylindrical entrance port of the monochromator, at a distance of twice its focal length from both the flame and the entrance slit. To further reduce the level of stray light reaching the detector, a conical, blackened light trap of 3 1/4 in diameter and 5 in length was placed on the opposite side of the flame. The photomultiplier tube was protected from RF and other sources of interference with a special housing designed for this purpose (see Table I or Reference 18). The burner/nebulizer assembly was a Perkin-Elmer unit, modified for use with a

Table I

Experimental Components and Manufacturers

Item	Type	Source
Monochromator	218	GCA/McPherson, Acton, Ma 01720
Photomultiplier	EMI 6256S	Gencom Div., Plainview, NY 11803
Photomultiplier Housing	1151	SSR Instruments, Santa Monica, Ca 90404 (now Princeton Applied Research, Princton, NJ 08540)
Amplifier/Discriminator	1120	SSR Instruments, Santa Monica, Ca 90404
Digital Synchronous Computer	1110	SSR Instruments, Santa Monica, Ca 90404
Nebulizer	303-0110	Perkin-Elmer, Norwalk, Ct 06852
Capillary Burner	--	Laboratory constructed
Xenon Arc Lamp	VIX 300 UV	EIMAC, Div. of Varian, San Carlos, Ca 94070
Lamp Power Supply (dc)	P150S-71	EIMAC, Div. of Varian, San Carlos, Ca 94070
Pulsed Power Supply	350	Velonex, Div. of Pulse Engineering, Inc. Santa Clara, Ca 95050
Function Generator	110	Wavetek, Inc., San Diego, Ca 92123

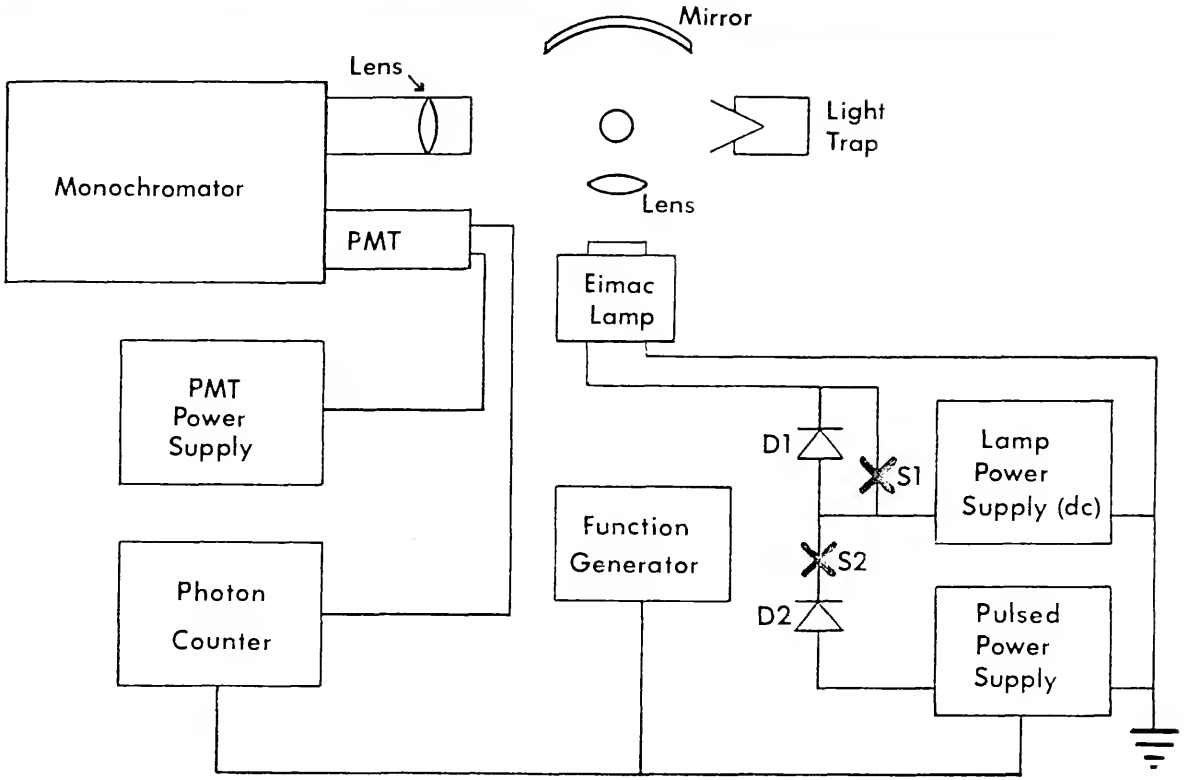


Figure 1. Schematic diagram of the experimental system employed for evaluation of the pulsed Eimac lamp. S1 and S2 are SPST knife switches; D1 = 1N3212, D2 = 1N4722.

capillary-type burner head (23) fitted with a collar designed to provide a sheathing gas around the flame (argon).

A 300 W Eimac xenon arc continuum source enclosed in a fan-cooled housing was used for excitation of atomic fluorescence. The lamp contains a built-in parabolic aluminum-coated reflector which reflects most of the emitted radiation through a 2.5 cm diameter sapphire window. Power supplied to this source consisted of periodic pulses superimposed upon a constant dc level. Power pulses were obtained from a Velonex High Power Pulse Generator with a plug-in output unit (No. V-1766) which delivers up to ± 120 V at high current levels. A conventional series-controlled, constant current dc power supply was employed to maintain a constant residual dc current flowing through the lamp while it was being pulsed.

The outputs of these two power supplies were wired in parallel as shown in Figure 1. Switch S_1 permitted protection of diode D_1 from the 15 kV starting pulse. Switch S_2 isolated the dc power supply from the pulse generator and was left open while the lamp was being started. S_1 was opened as soon as the arc had been initiated, and S_2 was closed immediately prior to switching on the pulse generator. The purpose of the diodes was to prevent reverse current surges.

The signal current (current pulses corresponding to individual photons) from the photomultiplier tube was passed

into an amplifier/discriminator module and then into a digital synchronous computer; these two instruments comprised the photon-counting system used in this study. The system contained two separate scalers (labeled DATA and BACKGROUND, respectively) and a variable sampling interval which could be synchronized with the excitation pulses from the Eimac lamp. In the mode of operation adopted for this work, the sampling gate was applied alternately to the signal produced during the "on" time of the excitation pulse and to the signal occurring between pulses. The former signal was collected in the DATA scaler, while the latter was collected in the BACKGROUND scaler. The outputs of the two scalers could be summed, subtracted, or presented individually. Thus, the contributions to the total signal of flame emission, photomultiplier dark current, and fluorescence generated by the residual lamp radiation between pulses could be subtracted out to obtain a pure pulse fluorescence (plus scatter) signal, while the summed outputs, recorded with distilled water being aspirated into the flame, could be used to estimate the noise on the background observed in fluorescence (see later).

The pulsed output of the high power pulse generator was synchronized with the photon counter data sampling gate by simultaneously triggering both instruments from a function generator, which was set to provide a 300 Hz square wave trigger signal. A gate triggering delay control

on the photon counter permitted the gate to be finely tuned to coincide with the lamp output pulse. A gate width or sampling period of 20 μs was applied to both scalers of the photon counter, while the pulse width of the lamp input pulses was fixed at approximately 14 μs (FWHM). These settings proved to be optimal in terms of overall system performance. Attempts to increase the pulse width sharply reduced the maximum usable pulse power, while further reduction in the photon counter gate width proportionately decreased its dynamic range, already severely restricted in the pulsed mode (as compared to operation in the cw mode; refer to the Results and Discussion section).

Procedure and experimental conditions. Experimental conditions used throughout this study are summarized in Table II. All components of the experimental system were operated according to the directions given in the manufacturers' manuals, except as otherwise noted (i.e., the pulsing of the Eimac lamp). The monochromator slit width, the observation height in the flame, and the argon-fuel-air ratio for the flame were established initially at values intended to represent a signal-to-noise compromise for all the elements and were held constant throughout the study.

The chemicals used in the preparation of stock solutions were all of reagent grade. All standard solutions employed in this work were obtained by serial dilution of the stock solutions.

Table II

Experimental Conditions for Present Atomic Fluorescence Studies

Monochromator	(0.3 m, Czerny-Turner, f/5.3 600 g/mm grating blazed at 3000 nm.)
Slit width	75 μm
Slit height	1 cm
Bandpass	0.4 nm
Dc Lamp Power Supply	
Current	6.5 A
Pulsed Power Supply	
Amplitude setting	≈ 1/2 of full scale
Pulse width	≈ 15 μs
Repetition rate	300 Hz
Flame Conditions (flow rates of gases)	
Air	9.7 ℓ/min
C_2H_2	1.3 ℓ/min
Ar	10 ℓ/min

Obervation height in flame, 2.5 cm (above burner top)

Photomultiplier voltage, 1115 V

Photon Counter gate width, 20 μs

The analytical calibration curve data presented here are based upon ten, 10 s measurements, while the precision data (% RSD) are based upon ten, 1 s measurements (ten, 10 s measurements resulted in an improvement of $\simeq \sqrt{10}$ in % RSD).

The detection limits were derived from the ten, 1 s measurements used for the determination of the % RSD data and were converted to detection limits corresponding to 10 s counting times; these values were obtained with solutions whose concentrations were roughly 10^2 times the detection limit for each element and were estimated by extrapolation to a signal equal to twice the noise on the blank.

Results and Discussion

In Table III, atomic fluorescence detection limits are given for 16 elements, along with values for comparison purposes obtained in a previous study (18) with a 500 W Eimac continuum source employed in the cw mode. When a photon-counting detection system is used and the major noise is shot noise, the RMS background (source-induced scatter, and emission and fluorescence of flame gas species) noise can be estimated with sufficient accuracy by taking the square root of the background signal obtained when distilled water is aspirated into the flame. For background shot noise to predominate, it must exceed ξ times the background, where ξ is the background flicker factor.

Table III

Limits of Detection Obtained for Several Elements in the Argon Separated Air/Acetylene Flame by Atomic Fluorescence Spectrometry with a Pulsed Continuum Source

Element	Wavelength, nm	Detection Limit, µg/ml	
		Pulsed Continuum Source (this work)	500 Watt Continuum Source[a] (reference)
Se	196.0	1	--
Zn	213.9	0.009	0.015
Cd	228.8	0.0014	0.006
Ni	232.0	0.02	0.025
Co	240.7	--[b]	0.015
Fe	248.3	--[b]	0.01
Au	267.5	0.2	0.15
Mn	279.5	0.003	0.002
Mg	285.2	0.0004	0.0001
Sn	303.4	1	0.5
Cu	324.7	0.004	0.0015
Ag	328.1	0.003	0.001
Pd	340.1	0.03	0.1
Cr	357.9	0.004	0.0015
Tl	377.6	0.01	0.006
Pb	405.8	0.03	0.05
In	451.1	0.01	0.025
Sr	460.7	0.003	0.0009

[a] Values for comparison purposes from Table IV, Reference 2. Experimental conditions are identical for each element.

[b] Noise due to background fluorescence resulted in analytically useless detection limits.

Thus, if the background flicker factor is about 0.003, typical for the Eimac-induced scatter background, then the total noise is predominantly background shot noise as long as the background count is below $\simeq 3 \times 10^4$ counts. The analytical calibration curves shown in Figures 2 and 3, as well as the relative standard deviations listed in Table IV, lend support to the general validity of this estimation.

The analytical calibration curves of Figures 2 and 3 reflect an important instrumental limitation associated with the utilization of a photon counter with a small duty factor. Because the maximum usable count rate is eventually limited by the pulse pair resolution of the photon counter, a restriction is imposed upon the total number of counts that can be recorded in a given measurement (time) interval without incurring an intolerably large counting error due to pulse overlap. If the actual photon-counting system "on" time is very much smaller than the measurement interval (small duty factor), the above restriction is proportionately more stringent. The "on" time duty factor for the system employed here was 0.006 (i.e., 20 μs times 300 gate intervals per second), and the instrumental pulse pair resolution was 12 ns. From these parameters, the practical upper limit on the total number of counts per 10 s measurement was estimated to be approximately 10^5 counts. Therefore, none of the analytical calibration curves were extended beyond

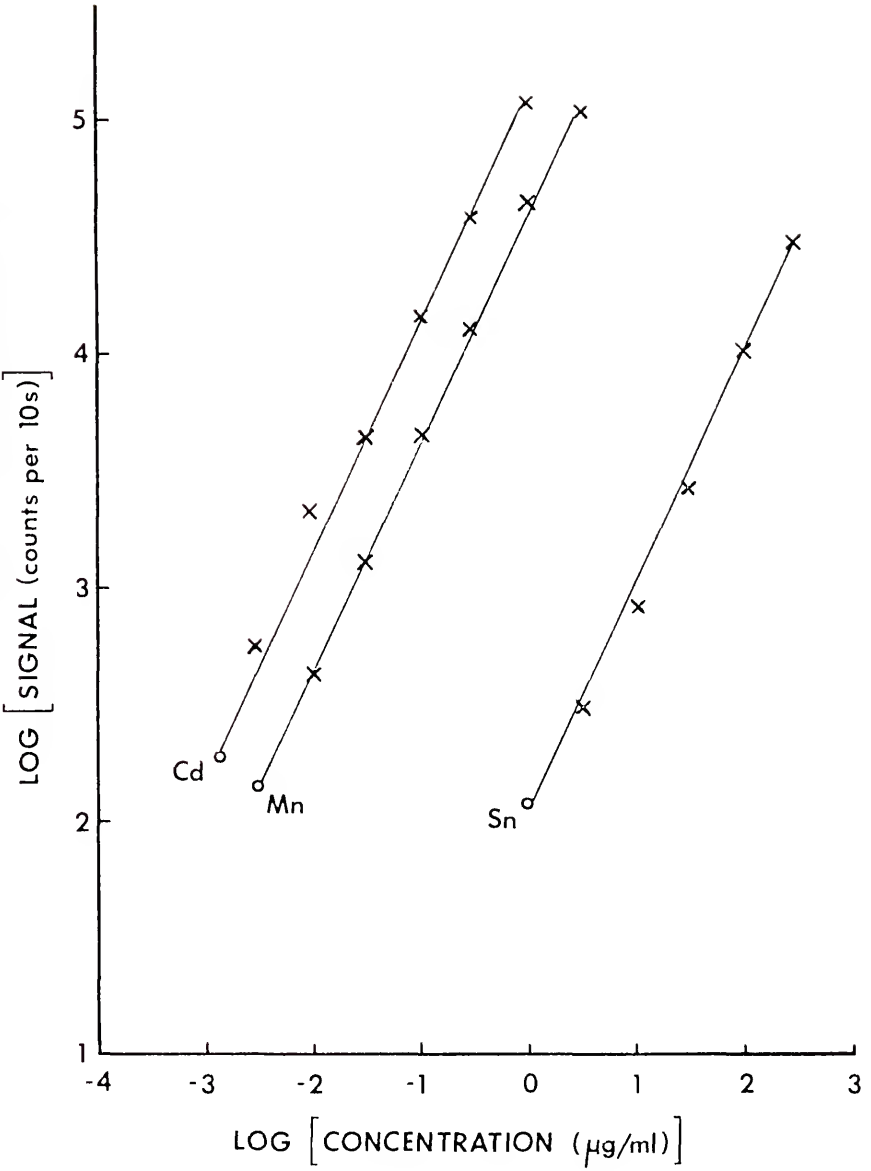


Figure 2. Analytical calibration curves for Cd, Mn, and Sn obtained with the pulsed Eimac source.

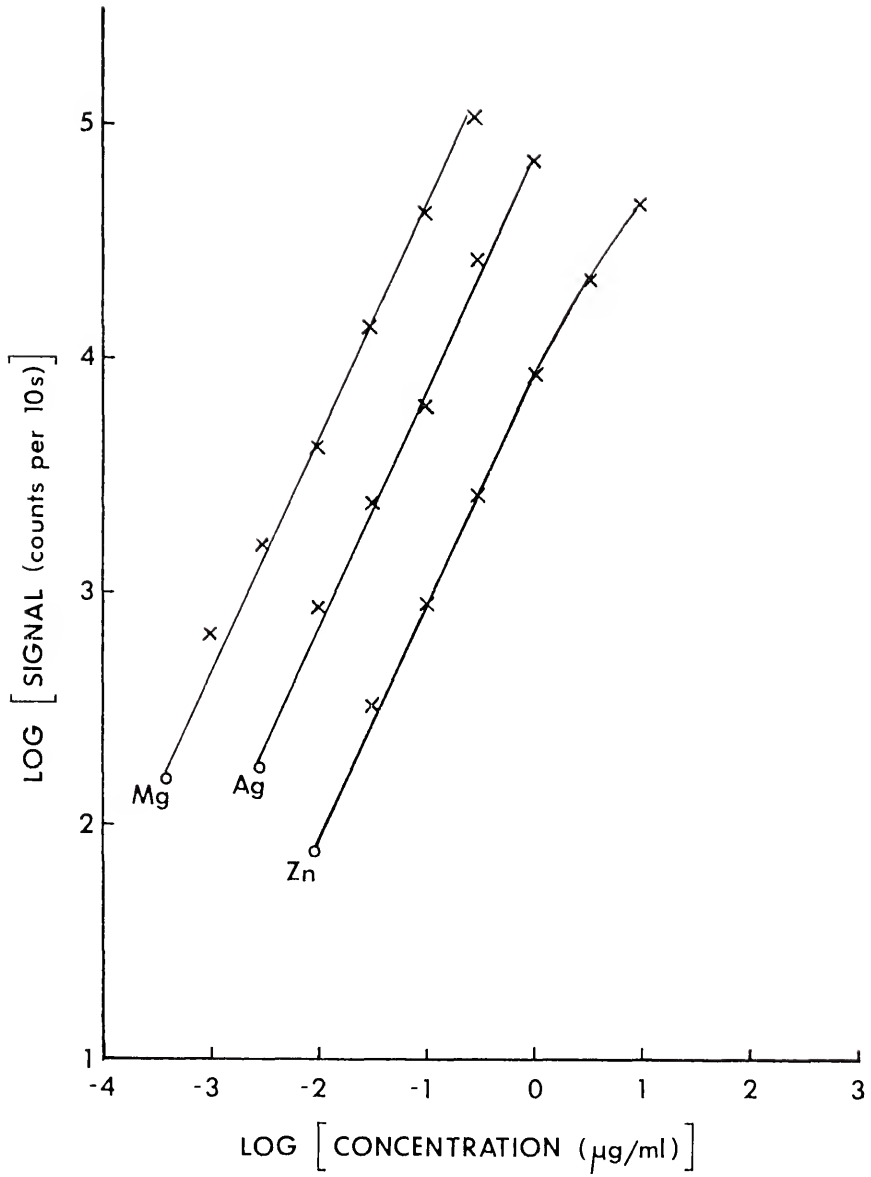


Figure 3. Analytical calibration curves for Mg, Ag, and Zn obtained with the pulsed Eimac source.

Table IV

Precision of Analytical Determinations of Several Elements by Atomic Fluorescence Spectrometry with a Pulsed Continuum Source

Element[a]	Average Background Signal, Counts/s	Relative Standard Deviation of Background (% RSD)	Relative Standard Deviation of Analyte Fluorescence Signal (% RSD)
Se	42	17.7	17.1
Zn	195	18.4	2.3
Cd	1233	3.7	7.2
Ni	626	6.4	7.9
Au	1126	5.0	2.8
Mn	465	6.0	1.9
Mg	1014	4.4	1.8
Sn	322	10.9	1.6
Cu	1294	3.4	2.1
Ag	1124	6.7	2.2
Pd	418	7.5	4.0
Cr	335	11.9	5.9
Tl	442	7.3	4.6
Pb	358	7.6	2.2
In	383	7.5	2.2
Sr	528	7.5	3.0

[a]Wavelengths of lines used here are those listed in Table III. Analyte concentrations were $\simeq 10^2$ times the detection limit for each element.

this level, even though the linearity limit due to self-absorption was not reached for any of the included elements, except possibly zinc. The linearity limit imposed by the photon counter can be increased by means of neutral density filters placed in the optical path to reduce the photon flux reaching the detector.

From Table III, it is apparent that limits of detection determined with the present pulsed system are roughly comparable to those obtained with the 500 W Eimac continuum source operated in the cw mode. That the expected improvement in detection limits largely failed to materialize is due primarily to the inherent instability of the Eimac lamp when operated in the pulsed mode, and to the unusually high level of background scatter radiation and/or molecular fluorescence observed during the "on" time of the pulse. A rather high residual dc current (6.5 A) was required to sustain the arc, even at moderate pulsing amplitudes. The total signal including atomic fluorescence generated by the flame and the source during a 20 μs interval between pulses was electronically subtracted from the same signal produced within the duration of the pulse. Moreover, the background signal occurring between pulses was added to the background signal associated with the pulse in order to determine the noise on the background (for detection limit calculations). Thus, the signal-to-noise ratio also depended upon the residual dc current flowing through the

lamp between pulses. Visible fluctuations in the lamp output intensity were observed at all but the lowest of pulse power settings, but the precision data of Table IV suggest that the noise amplitude in many cases was not significantly greater than that which is expected from a shot noise limited measurement system; consequently, these source fluctuations must not have contributed significantly to the total noise at the signal levels used to determine the precision data. The background fluorescence and scatter signals observed with the present pulsed system were substantially larger than those seen in previous cw studies, and this fact is believed to represent an important limitation with respect to signal-to-noise ratio in the present study.

The reasons for the unusually large background signal observed as fluorescence cannot be clearly ascertained with the instrumental system used for this work. However, there is little room for doubt that, at any given wavelength, scattering of the incident source radiation from particles or molecules in the flame accounted for a significant proportion of the total background signal. It should be noted that several previous studies (17,19,22) of atomic fluorescence excited by a continuum source have reported little or no evidence of scatter when the argon separated air-acetylene flame was used.

The phenomenon of light scatter is not sufficient, however, to explain the substantial irregularity observed in the spectral distribution of the background radiation. Scattering of source radiation might be expected to produce some contour in the background spectrum if the spectral distribution of the source radiation contained prominent emission lines and bands superimposed upon the emitted continuum. Preliminary studies of the spectral output of the pulsed Eimac lamp have indicated that a structured spectrum of this type is indeed emitted. Nevertheless, many of the most prominent anomalous features in the background spectrum are known or suspected to have resulted from the fluorescence of molecular species in the flame. In a series of experiments conducted prior to this study, the molecular fluorescence bands occurring between 230 and 270 nm (22) were tentatively linked to the PO molecule. Apparently, PO is formed in the flame from an impurity in one of the flame gases, probably the PH_3 impurity in acetylene (20). As a part of this study, a 0.33 M H_3PO_4 solution was aspirated into the flame and was found to increase the PO fluorescence intensity by a factor of three. These bands interfered so extensively with the determinations of Co at 240.7 nm and Fe at 248.3 nm that useful detection limits for these elements could not be determined at these wavelengths. Similar interferences are believed to have occurred elsewhere in the spectrum. Indeed,

the observed background irregularities due to source scatter and/or molecular fluorescence were of sufficient magnitude and number to cause possible error if off-wavelength correction for the background were attempted in multielement analysis as described in Reference 18.

Cursory observations of the spectral radiant intensity of the Eimac lamp have indicated a shift in the source output toward the UV resulting from the pulsing of the lamp. However, the background interferences discussed above were most apparent in the short-wavelength portion of the spectrum, and these appeared to nullify any improvement which might otherwise have been expected in the detection limits of elements with resonance lines at low wavelengths. Operation of the Eimac source in the pulsed mode did not seriously decrease the useful lifetime of the source (the present lamp has been operated for more than 200 h with no apparent loss in light output and little observable deterioration of the arc electrodes). Moreover, no RF or ground-loop-type interference was experienced with the system as employed in this work.

CHAPTER III

THE SPECTRUM OF THE FLUORESCENCE BACKGROUND

In the previous chapter, in which a pulsed Eimac continuum source was evaluated for application to atomic fluorescence spectrometry, it was noted that the background spectrum, i.e., the fluorescence signal observed at each wavelength when only distilled water was aspirated into the flame, contained numerous "anomalies" which resulted in sharply elevated background levels at certain wavelengths of interest. It was recognized that these background spectral irregularities could be attributed to either of two phenomena: (a) molecular fluorescence of molecules within the flame, and/or (b) prominent peaks in the source spectral output, transferred to the detector by scattering of source radiation from particles and molecules in the flame. Some of these background anomalies were known to have resulted from molecular fluorescence; however, many others had never been observed previously and thus could not be described. Because of the discrete nature of the digital output signal of the photon-counting system and the lack of a suitable digital-to-analog converter, it was not feasible in the work of Chapter II to scan the entire

background fluorescence spectrum over the range of wavelengths utilized for multielement atomic fluorescence measurements.

Although molecular emission (24-27) and absorption (27-29) of flame gas constituents have been fairly well documented, and their effects upon analytical atomic fluorescence measurements recognized (4,13,30), molecular fluorescence in flames has received but little attention in the literature. The fluorescence of the CH radical at 431.5 nm has been excited by a dye-laser in an oxyacetylene flame (31), and several observations of OH flame fluorescence have been reported (3,32,33). Molecular fluorescence bands were seen, but not identified, by Johnson, Plankey, and Winefordner (22). The fluorescences of several alkaline earth compounds (CaOH, SrOH, and BaCl) have been observed when concentrated solutions of these compounds were aspirated into flames irradiated by high intensity continuum sources (34,35).

Reported incidences of observable scatter signals in atomic fluorescence studies have been linked primarily to the use of cool flames and sample matrices with high solids content (18,36,37). Measurable scatter signals have, in general, not been noted when pure aqueous solutions were used with the air-acetylene flame.

For these reasons, a study of the background anomalies described in the previous chapter has been conducted and is

discussed here. Wherever possible, the equipment and experimental conditions used in the work of the previous study (Chapter II) have been retained in the present work in order to preserve the validity of any comparisons which may be drawn.

Experimental

Instrumental systems (see Table V). Block diagrams of the experimental systems used in the present work are given in Figures 4-6. The excitation source, nebulizer, burner, monochromator, photomultiplier detector (and its shielded housing), mirror, light trap, and entrance optics are exactly as used in the work of the previous chapter. For fluorescence measurements in the pulsed mode, the experimental arrangement of Figure 4 was adopted; this arrangement is similar to the one used previously (see Figure 1) except that a boxcar integrator and strip-chart recorder perform the signal-processing functions for these studies. Figure 5, the system used here for the fluorescence measurement in the cw mode, is similar to Figure 4 except that a lock-in amplifier is used in place of the boxcar integrator, and the excitation optics have been altered to accommodate a mechanical chopper in the excitation beam. In addition, the lamp power supply employed for all cw measurements was a series-controlled, constant current dc power supply similar to the one described in the previous

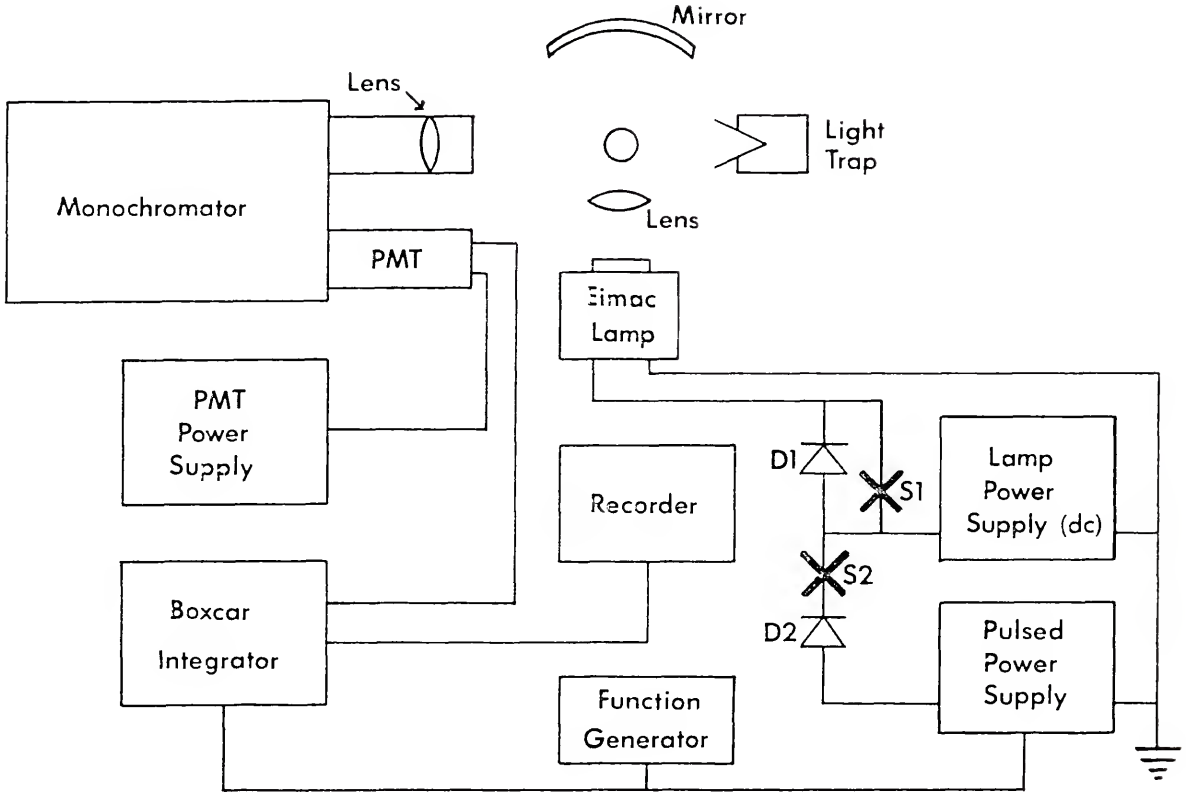
Table V

Experimental Components and Manufacturers

Item	Type	Source
Boxcar Integrator/Integrator Modules (A & B)	162/164	Princeton Applied Research, Princeton, NJ 08540
Lock-in Amplifier	391	Ithaco, Inc., Ithaca NY 14850
Current Preamplifier	164	Ithaco, Inc., Ithaca NY 14850
Strip Chart Recorder	SRG	Sargent-Welsh Scientific, Birmingham, Al 35202
Lamp Power Supply (dc)	PS 300-1	Eimac, Div. of Varian, San Carlos, Ca 94070
Acetylene (PH_3) Filter	--	L'Oxhydrique Francaise, Malakoff, Paris, France
Mechanical Chopper	--	(Laboratory constructed)

Note. All other instruments used in this study are listed in Table I.

Figure 4. Schematic diagram of the system used for all flame background molecular fluorescence measurements in the pulsed mode. Switches and diodes are as described previously (Figure 1).


Mirror
Lens
Monochromator
Light
Trap
Lens
PMT
Eimac
Lamp
PMT
Power
Supply
Recorder
D1
S1
Lamp
Power
Supply (dc)
S2
D2
Boxcar
Integrator
Pulsed
Power
Supply
Function
Generator

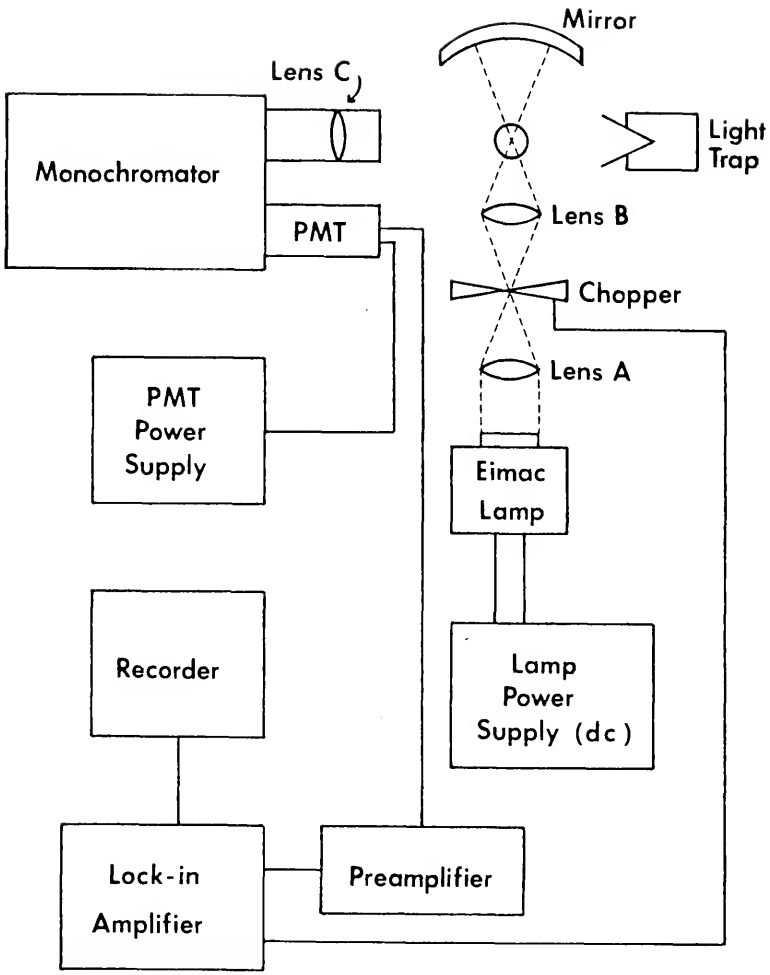
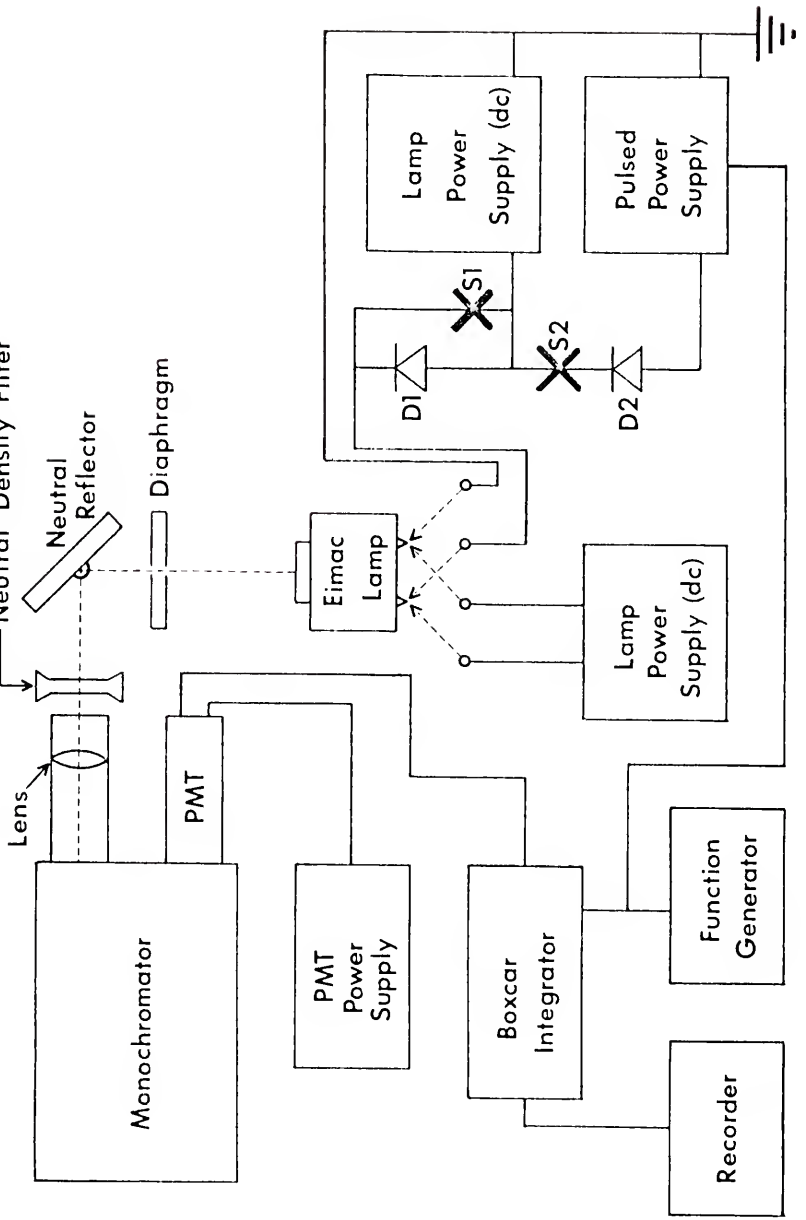


Figure 5. Schematic diagram of the system used for the measurement of flame background molecular fluorescence in the cw mode.

Figure 6. Schematic diagram of the experimental arrangement employed for the measurements of the lamp spectral output. Note that either the cw or the pulsed power supply circuit can be attached to the lamp input terminals.


Neutral Density Filter
Neutral Reflector
Diaphragm
Eimac Lamp
Lamp Power Supply (dc)
Pulsed Power Supply
S1
S2
D1
D2
Lens
PMT
Monochromator
PMT Power Supply
Boxcar Integrator
Function Generator
Recorder

chapter. It should be noted that the optical configuration of Figure 5 is not the optimum arrangement for chopped beam-cw source measurements; the system can be optimized, in principle, only when (for lenses of equal diameter) the focal length of lens A is twice that of lens B, or (if the focal lengths are equivalent) when the diameter of lens B is twice that of lens A. In the system of Figure 5, lenses A and B have equivalent (2 in) focal lengths and diameters, and despite adjustments in their positions to achieve the best possible result, significant light losses were encountered. However, these losses did not detract from the validity of the background recordings of this work, since an optimized system was not required to observe the characteristics and features described in this study.

For all measurements except that of fluorescence in the cw mode, signal processing was accomplished with a dual-channel boxcar integrator whose output was fed to a strip-chart recorder. The dual-channel boxcar integrator employed for these studies was equipped with two separate integrator modules labeled A and B, respectively, a variable aperture or sampling interval applicable simultaneously to both integrators, and a separate aperture delay circuit for each integrator module. The aperture delays are referenced to a single trigger signal supplied externally; hence the instrument is capable of being synchronized to the excitation pulse in the pulsed mode by simultaneously triggering

both the boxcar and the pulsed power supply from the same trigger source. The outputs of the two integrators can be read individually or can be subtracted electronically to yield the difference signal, A - B. With the aid of an oscilloscope, the aperture of the A integrator was set (using the aperture delay control) to coincide with the lamp output pulse (for pulsed mode measurements) and the aperture of the B integrator was positioned at a point in time approximately half-way between successive A integrator apertures. Therefore, the total signal fed into the A integrator consisted of flame emission signal plus photomultiplier dark current plus any signal (fluorescence and/or scatter) generated by the source output pulse, while the total signal processed by the B integrator consisted of flame emission signal plus photomultiplier dark current plus any fluorescence and/or scatter signal produced by the residual lamp output between pulses. Hence, the difference signal, A - B, was composed entirely of fluorescence and scatter signals produced by the lamp output pulse (as in the previous study), and it was this net signal which was recorded in all spectra obtained in the pulsed mode. As in the work of the previous chapter, the aperture was chosen to be 20 μs, and the excitation source pulse width was fixed at approximately 15 μs. A time constant of 0.8 s was employed for all work with the boxcar integrator.

For the measurement of fluorescence in the cw mode, the signal was processed with a lock-in amplifier, together with a current preamplifier whose function was to amplify the signal current and convert it to a signal voltage for use at the imput terminal of the lock-in. The reference channel of the lock-in was supplied with a reference output triggering signal from the chopper. The sensitivity was adjusted to achieve the desired response, and the time constant was set at 0.4 s. The output of the lock-in was fed to the same strip-chart recorder as employed with the boxcar integrator.

To record the spectral distribution of the excitation source radiation in both the pulsed and cw modes, the experimental system was modified as shown in Figure 6. An aluminum block coated with Eastman White Reflectance Coating no. 6080 (Eastman Kodak Co., Rochester, N.Y. 14650) was placed on top of the burner assembly and oriented so as to scatter the source radiation into the monochromator. The coating contained barium sulfate, and when applied according to the manufacturer's directions, it formed a diffuse reflector whose absolute reflectance is 90% or better at all UV and visible wavelengths above 220 nm (38). To reduce the radiant flux impinging on the photomultiplier, a 2.0 neutral density filter was placed in front of the monochromator entrance port, and a diaphragm with a 0.5 cm aperture was positioned between the source and the

reflector at a distance of 6 cm from the reflector. The distance from source to reflector was approximately 30 cm. As shown in Figure 6, either the pulsed or cw lamp power supply could be attached to the lamp input terminals, as required.

Procedure and experimental conditions. A summary of the experimental conditions applicable to this work is given in Table VI. All equipment was operated as described in the manufacturers' manuals except as previously noted. The monochromator slit width and the observation height in the plane were chosen to be identical to those used in the previous study (Chapter II).

When required, the acetylene filter (for removal of PH_3) was spliced into the acetylene supply line between the pressure regulator on the acetylene tank and the flow control value. In all fluorescence studies, distilled water was aspirated into the flame.

For recording the lamp spectral distribution using the experimental arrangement of Figure 2, all instrumental settings were maintained identical to those used for the fluorescence studies, except that the signal recorded in the cw mode was the output signal from the A integrator only, rather than the difference signal, A - B. Thus, the boxcar integrator was gated with a repetition frequency of 300 Hz and an aperture width of 20 μs in both the pulsed and cw modes; this was done to permit a more direct comparison of the lamp outputs in the two modes.

Table VI

Summary of Experimental Conditions

Monochromator	
Slit width	75 μm
Slit height	1 cm
Bandpass	0.4 nm
Spectral scan rate	5 nm/min
Lamp Power Supply (dc) (used in pulsed power circuit)	
Current	6.5 A
Lamp Power Supply (dc) (used in cw studies)	
Current	20 A
Pulsed Power Supply	
Amplitude setting	~ 1/2 of full scale
Pulse width	~ 15 μs
Repetition rate	300 Hz
Flame conditions	
Fuel-lean	Air 10.5ℓ/min C_2H_2 1.3ℓ/min Ar 10 ℓ/min
Fuel-rich	Air 9.0ℓ/min C_2H_2 1.3ℓ/min Ar 10 ℓ/min
Stoichiometric	Air 9.7ℓ/min C_2H_2 1.3ℓ/min Ar 10 ℓ/min

Table VI (continued)

Strip Chart Recorder chart speed	1 in/min
Photomultiplier voltage	-1400 V
Boxcar Integrator aperture	20 μs
Observation height in flame	2.5 cm above burner top

Results and Discussion

The spectra recorded for this study are shown in Figures 7-13. In each case, the baseline (the horizontal axis) represents the photomultiplier dark signal, i.e., the signal observed with the monochromator slits closed. The series of bands lying in the 220-275 nm region of the fluorescence spectra (Figure 7-11) constitute the γ-system of the PO molecule, arising from the electronic transition $A^2\Sigma$-$X^2\Pi$. The weak band in the 280-295 nm portion of the spectrum of Figure 7, as well as the much stronger band in the 305-320 nm region, are both due to the OH radical. This system, known only as the 306.4 nm system of OH, is due to the transition $A^2\Sigma^+$-$X^2\Pi$. The peak or sharp band at 336 nm is probably the band head of the 336.0 nm system ($A^3\Pi$-$X^3\Sigma$) of the NH radical. Interference of this band with atomic fluorescence measurements is, of course, unlikely because of its narrowness. The band whose maximum is at 388.3 nm is believed to be due to the cyanogen violet system, i.e., the $B^2\Sigma$-$A^2\Pi$ transition of the CN radical. Another possibility for this assignment, although considered less likely, is the 390.0 nm system of CH. However, this band is described (27) as being degraded to the red and having maxima at 397.1 and 388.9 nm. Of these characteristics, only a "secondary" maximum at 387.1 nm is evident, which suggests only that the observed fluorescence in this spectral region may contain a contribution from both species.

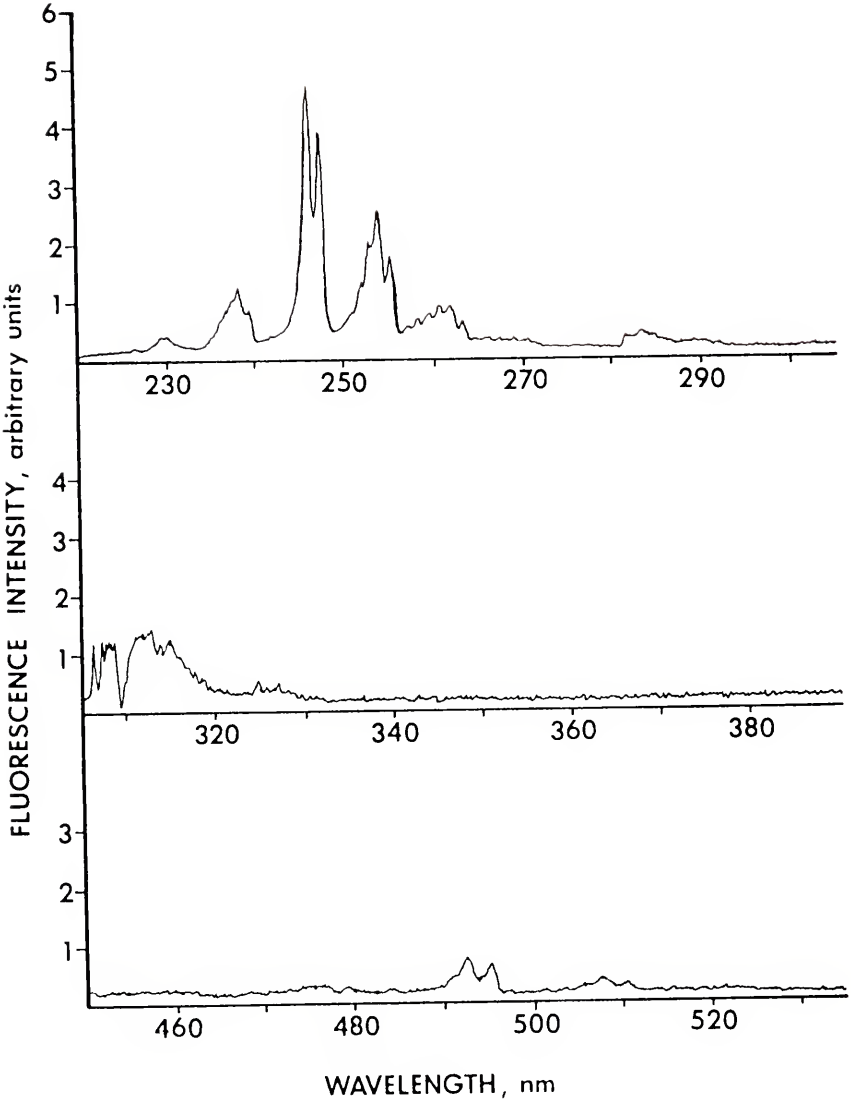


Figure 7. Flame background molecular fluorescence spectrum obtained in the pulsed mode from a fuel-lean flame. The portions of the 190-600 nm spectral region which are not shown here contained no detectable molecular fluorescence.

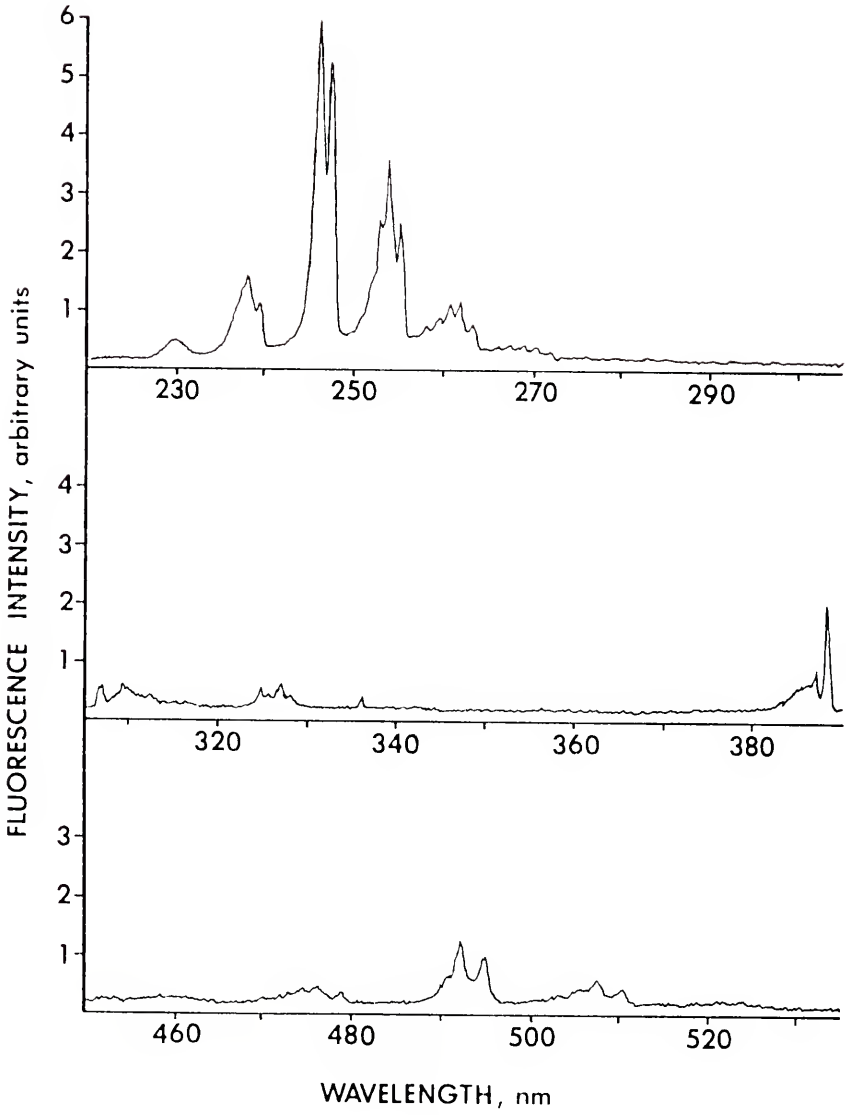


Figure 8. Flame background molecular fluorescence spectrum obtained in the pulsed mode from a fuel-rich flame. As in Figure 7, only selected portions of the spectrum are shown.

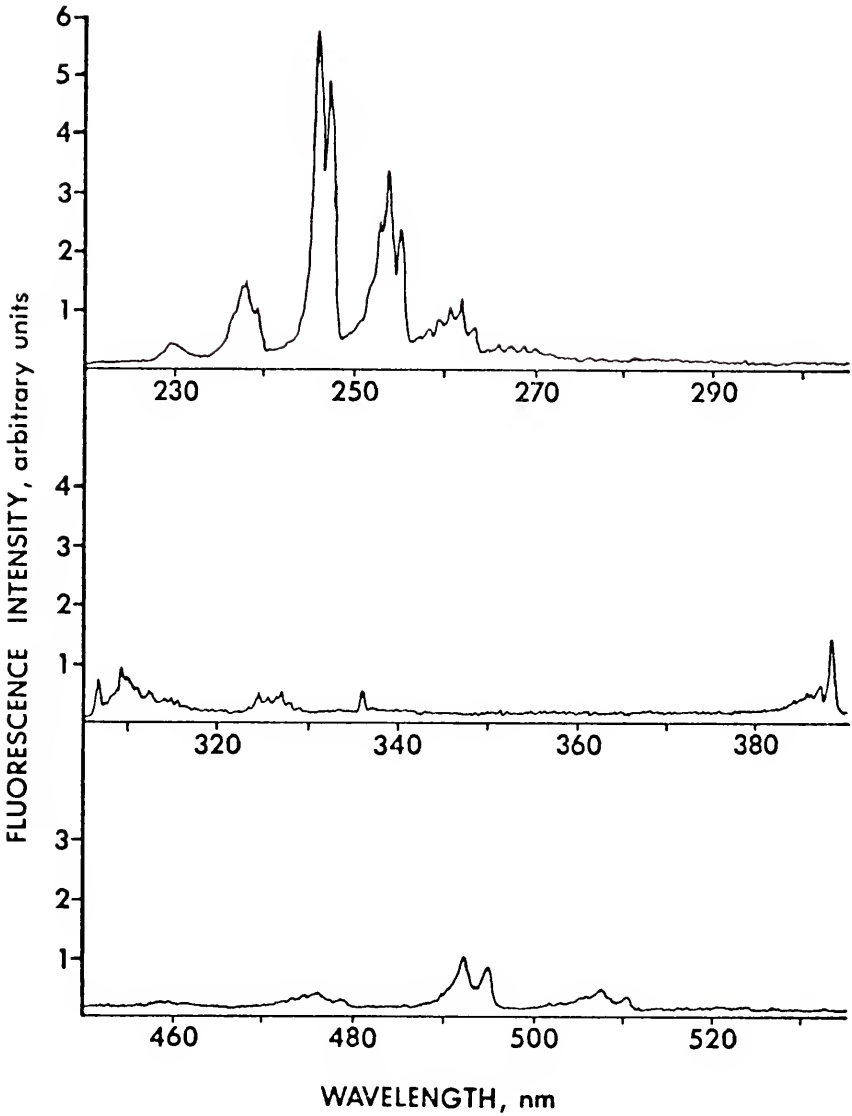


Figure 9. Flame background molecular fluorescence spectrum obtained in the pulsed mode from a stoichiometric flame. As in Figure 7, the barren portions of the 190-600 nm spectral region have been excluded.

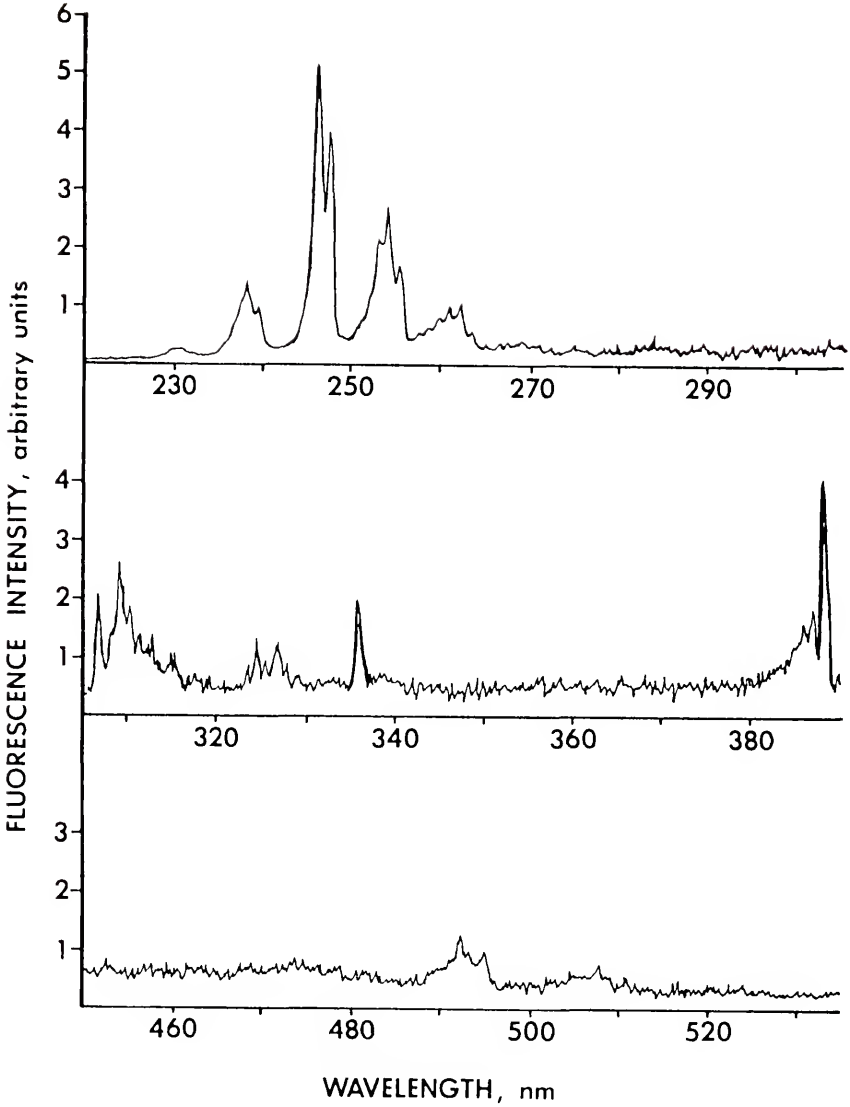


Figure 10. Selected portions of the flame background molecular fluorescence spectrum obtained in the cw mode with a stoichiometric flame.

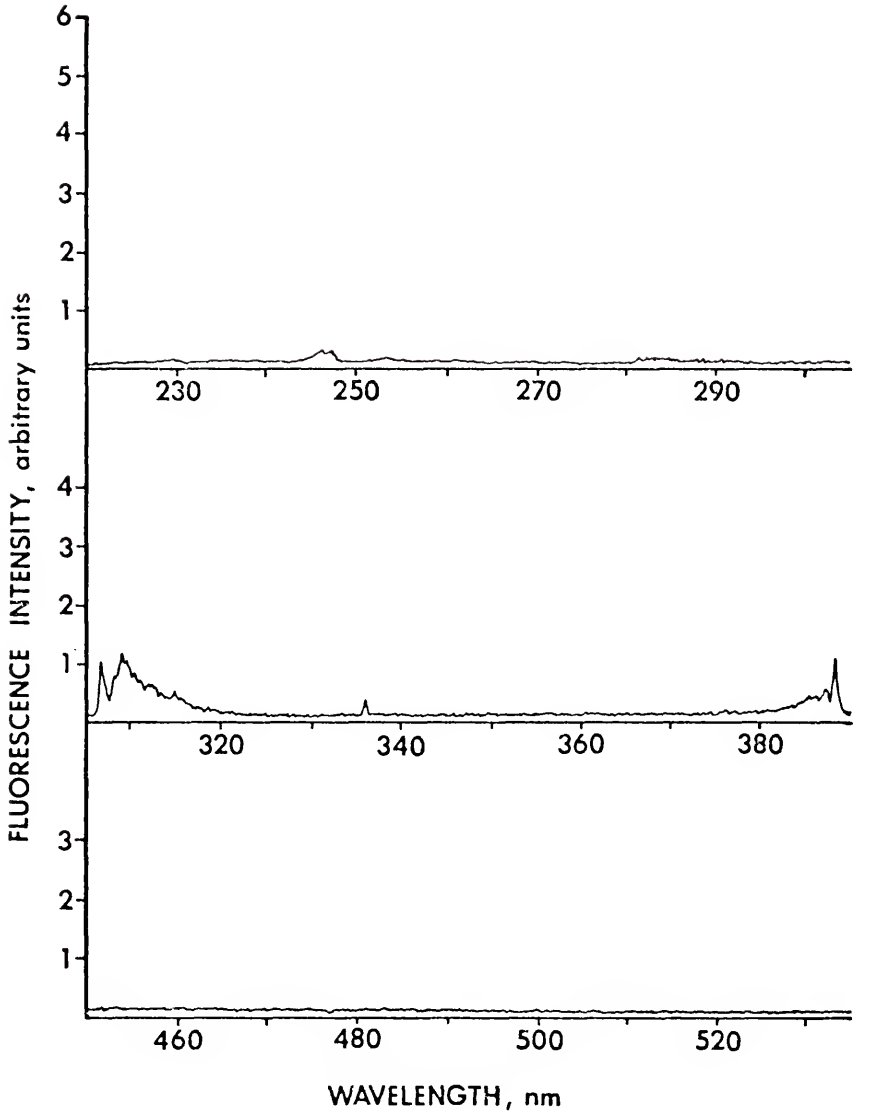


Figure 11. Selected portions of the flame background molecular fluorescence spectrum obtained in the pulsed mode from a stoichiometric flame while employing the acetylene filter (for removal of PH_3) as described in the text.

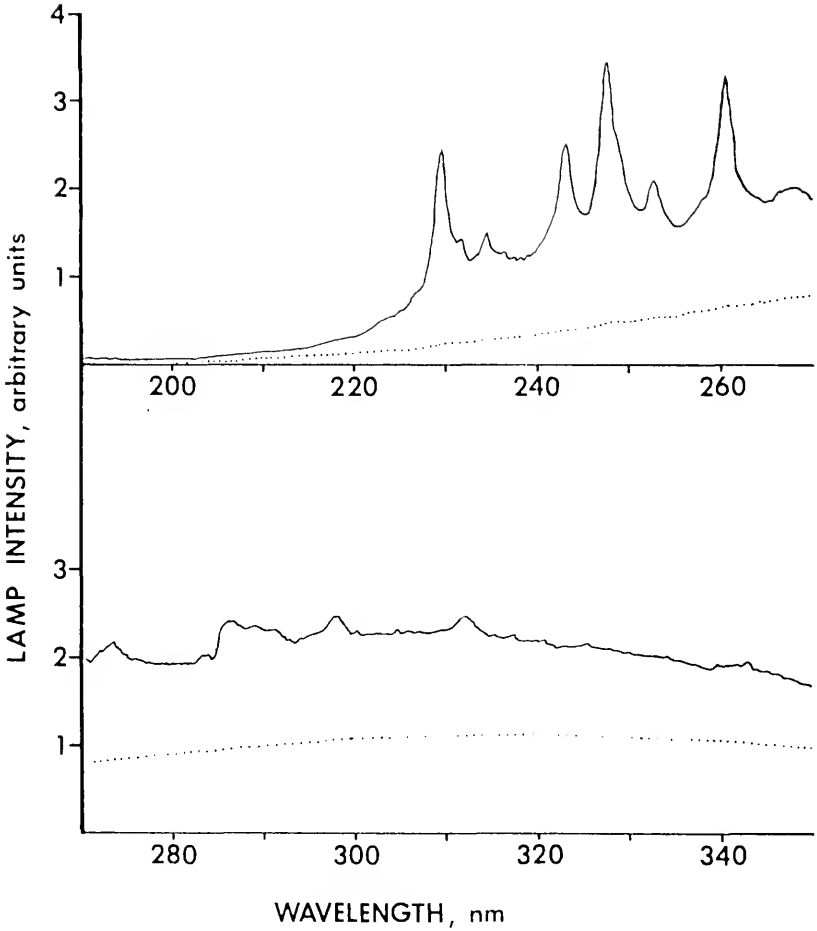


Figure 12. Lamp spectral output in the 190-350 nm wavelength region of the Eimac lamp operated in the pulsed (solid line) and cw (dotted line) modes.

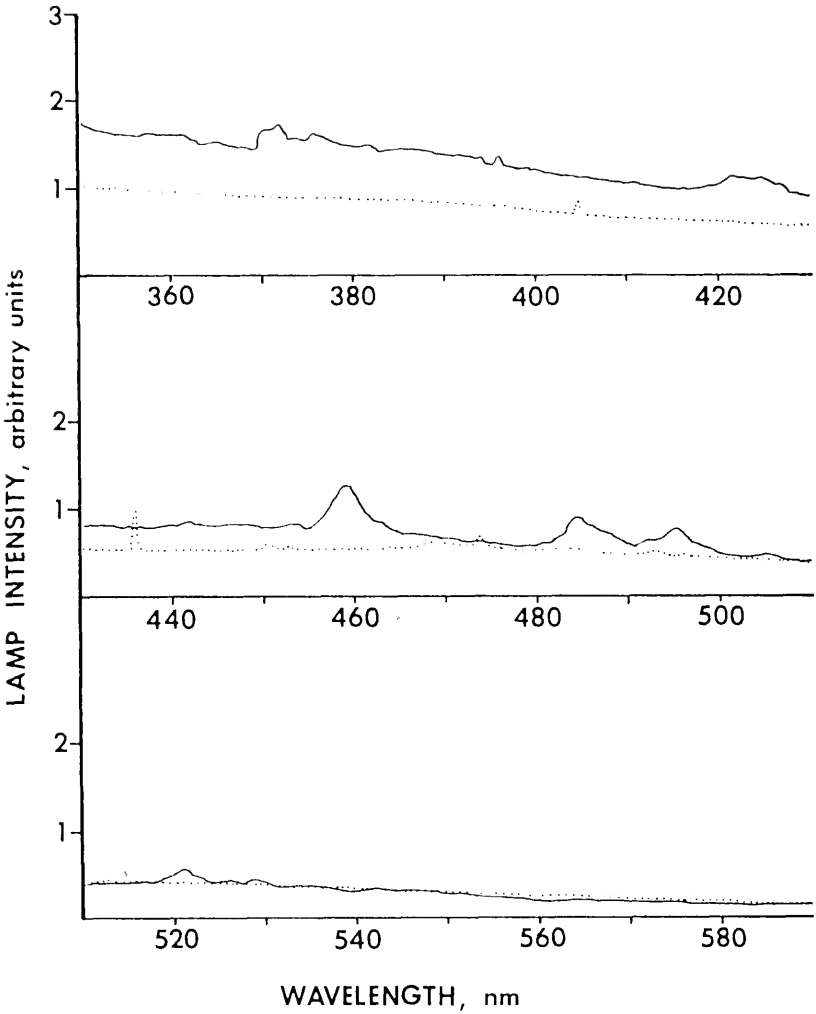


Figure 13. Lamp spectral output in the 350-590 nm wavelength region of the Eimac lamp operated in the pulsed (solid line) and cw (dotted line) modes.

The series of bands observable beyond 450 nm are the grating second-order dispersion of the PO γ-system bands. Although observed in second order, these features are nonetheless capable of adverse influence upon atomic fluorescence measurements in this spectral vicinity. The above band assignments are summarized in Table VII.

At any wavelength in the fluorescence spectra which is well removed from the observed bands, the offset between the baseline and the spectral trace represents the scatter signal at that wavelength. There are no "anomalies" in any of these spectra which can be shown to correspond to peaks in the spectral distribution of the lamp radiation, as had been suspected previously. However, a scatter signal is obviously present at all wavelengths and in atomic fluorescence spectrometry with a continuum source may ultimately limit the signal-to-noise ratio for many analyses, as it did in the previous study. In spite of these results, it may still be possible to observe peaks in the fluorescence background, transmitted from the source by scatter, in those applications of the pulsed Eimac source where scatter signals are found to be large.

An important objective of this study was to effect a comparison of the results obtained with the Eimac source operated in the pulsed and cw modes, respectively. Figure 9 is the pulsed mode fluorescence spectrum which most closely corresponds to the cw mode fluorescence spectrum of Figure 10. The fluorescence of the γ-system of PO is clearly more

Table VII

Summary of Molecular Fluorescence Band Assignments

Spectral Region (nm)	Species	Transition	Spectroscopic System
220-275	PO	$A^2\Sigma-X^2\Pi$	γ-system
280-295	OH	$A^2\Sigma^+-X^2\Pi$	306.4 nm system
305-320	OH	$A^2\Sigma^+-X^2\Pi$	306.4 nm system
323-330	PO	$B^2\Sigma-X^2\Pi$	β-system
336 (max)	NH	$A^3\Pi-X^3\Sigma$	336.0 nm system
380-390	CN	$B^2\Sigma-A^2\Pi$	cyanogen violet system
450-550	(PO γ-system grating second order)		

intense (relative to the fluorescence signals of OH, NH, and CN) in the pulsed mode than in the cw mode; an apparent reason for this can be discerned from Figures 12 and 13. Not only is the spectral output of the pulsed lamp generally shifted toward the UV as compared to that of the cw source, but also many of the large peaks in the pulsed lamp spectrum coincide with the bands of the PO γ-system. Hence, the fluorescence excitation of this molecular band system is more efficient in the pulsed mode.

Comparing Parts A and B of Figures 12 and 13 further, it can be seen that the lamp output in the pulsed mode during the 20 μs sampling period is only a little (~ 3 to 5 times) larger than the lamp output in the cw mode during the same sampling period. Considering that practical analytical atomic fluorescence measurements employing a continuum source in the cw mode utilize a much larger duty factor and more efficient excitation optics, the above fact must have played a significantly negative role in the previous study, in which detection limits obtained in the pulsed mode were compared to those obtained in the cw mode, with little or no improvement evident for the pulsed mode. The reasons for this less-than-favorable intensity ratio are not completely understood at this time; apparently the peak level of radiation emitted during the application of the power pulse represented an excessively small fraction of the peak electrical power dissipated within the "on"

time of the pulse. Because accurate current measurements cannot be made by conventional means in a low-resistance, high-current circuit, and because the resistance of a xenon arc does not obey Ohm's Law, it was not feasible to measure the power input to the pulsed source.

It is interesting to compare Figures 7-9 to ascertain the effect of varying the fuel/air ratio upon the observed fluorescence bands. The absence, in the fuel-lean flame, of the bands assigned to CN and NH is striking. Also, the OH band at ~285 nm is present to a significant extent only in the fuel-lean flame, and even the band at ~310 nm appears to undergo a marked increase in intensity as the fuel/air ratio is decreased. Further scrutiny of the latter band reveals that, at the wavelengths corresponding to fluorescence maxima in the stoichiometric and fuel-rich spectra (Figures 9-11 at 306.8 nm and 309.2 nm), there are sharp "dips" indicating virtually no fluorescence at all in the fuel-lean flame. Although these particular observations may have little immediate relevance to the study of molecular fluorescence as a potential source of interference in atomic fluorescence spectrometry, they do reveal that molecular fluorescence in flames may be, in many instances, strongly dependent upon flame conditions, a fact which could be of considerable importance in optimizing experimental conditions for analysis by atomic fluorescence spectrometry.

The fluorescence spectrum of Figure 11 was recorded under the same set of experimental conditions as adopted for the spectrum of Figure 9, except that the acetylene filter for removal of PH_3 was inserted into the acetylene line immediately prior to recording the spectrum of Figure 11. The fluorescence of the γ-system of PO is barely discernible in Figure 11, indicating the excellent filtering capability for the filter used here. Moreover, the grating second-order bands above 450 nm have disappeared entirely. These spectra suggest that the "attenuation factor" for this filter may be as much as 30 or more (based upon relative peak heights).

At this point, it is appropriate to consider in general terms what effects these findings may have on multielement analysis by atomic fluorescence spectrometry with a continuum source. In applications where it is desired to obtain a qualitative scan of the entire fluorescence spectrum in order to establish the presence or absence of various metals within a sample, molecular fluorescence bands could easily obscure the presence of an atomic line. However, a detailed knowledge of the molecular fluorescence background associated with the particular analytical conditions (sample matrix, flame gases, flame conditions, impurities, etc.) relevant to the analysis should be effective in minimizing any such spectral interferences.

The effect of molecular fluorescence upon quantitative multielement analysis is a more complex matter. Because a molecular fluorescence band which overlaps an atomic fluorescence line constitutes an additional component of light viewed by the detector at that wavelength, it is reasonable to expect an increase in the shot noise amplitude at the output of the photodetector as a result of any spectral interference from molecular fluorescence. Moreover, molecular fluorescence is capable of transmitting source fluctuations to the detector, should source flicker noise prove to be significant in relation to the total observed noise level in the system. In these ways, interference from flame molecular fluorescence is, in principle, similar to that associated with source radiation scattering from flame components, except that molecular fluorescence is usually localized spectrally, and off-wavelength correction for it may prove to be difficult or impossible (as mentioned previously).

An additional noise component may become significant for some types of molecular fluorescence. It has been demonstrated in this study that at least some molecular fluorescence bands display an extremely high sensitivity to flame conditions, specifically the fuel/air ratio. Furthermore, it is possible, indeed likely, that the fluorescence of these species may display a strong dependence upon the location in the flame of the focused source radiation (taken here to be equivalent to the object

volume element, within the flame, of the monochromator entrance optics). Therefore, any general instability or turbulence associated with the flame may lead to measurable fluctuations in the intensity of the molecular fluorescence of these species.

If a fluorescing molecular species is introduced into the flame by the aspiration of a real sample containing that species (or its precursor), then the molecular fluorescence should interfere directly with any overlapping atomic fluorescence line employed for elemental analysis and thus cause a proportional quantitative error in the measurement. Correction for this type of error would depend upon a knowledge of the concentration of the interfering molecular species (or its precursor) in the sample matrix, as well as the concentrations of any concomitants affecting the molecular fluorescence intensity, either positively or negatively.

It should be noted that the total effect on atomic fluorescence measurements of the presence (or absence) in the flame of any fluorescing molecular species cannot be established solely from a knowledge of the fluorescence characteristics of that species, because the absorption and emission properties of that species also affect the signal-to-noise ratio (5,13,30) for atomic fluorescence measurements at any wavelengths susceptible to interference from the molecular bands(s).

CHAPTER IV

FURTHER CHARACTERIZATION OF THE FLUORESCENCE OF PO

In spite of the increasing development of atomic fluorescence spectrometry (39), there have been few studies on molecular fluorescence of species in flames, as indicated previously. It has been suggested (35) that molecular fluorescence might be applied to the analysis of non-metallic elements, such as sulfur, phosphorus, carbon, nitrogen and the halogens, which are difficult to determine by atomic fluorescence because their atomic resonance lines are in the far or vacuum UV. However, molecular spectroscopic methods have been used previously for the analysis of non-metallic elements in flames only via molecular emission (40) and absorption spectrometry (41,42). Emission intensities of molecular species in flames are often as high as or higher than the flame emission intensities of atoms (43), and it is well-known that the study of molecular absorption flame spectroscopy yields important information about molecular species (44-47), background absorption (48,49), chemical interferences in atomic absorption spectrometry (50-52), and kinetics and mechanisms of flame reactions (53). Therefore, studies of molecular fluorescence in flames from the points of view of spectroscopists

and analytical chemists are of interest and so have been carried out in the present work. The fact that the molecular fluorescence bands of PO were found to constitute a serious source of interference in atomic fluorescence spectrometry represents an added incentive for this work.

During the past five years, a number of TV-type multichannel detectors have been evaluated for application to analytical atomic spectrometry (54-62). Among these devices, silicon diode array vidicon camera tubes [or silicon intensified target (SIT) tubes] combined with an optical multichannel analyzer (OMA) have been used as detectors for atomic emission (58,60,62), absorption (57,59) and fluorescence spectrometry (62). The SIT-OMA system has a number of advantageous characteristics, including a wide spectral range (200-1100 nm), high quantum efficiency (>50% in the range 350-800 nm, >20% in the range 250-100 nm), linear response over a large range of fluxes ($\sim 10^3$), low geometric distortion, feasibility of data storage, and capability of subtraction of the background in the spectra. These characteristics are considered in order to propose the possibility that the SIT-OMA system might be judiciously applied to the study of molecular flame spectroscopy. In general, molecular spectra are broad and weak, and contain a great deal of coincident background radiation due to the various co-existing species in the flame or matrix. Therefore, signal averaging of the

data (to obtain better signal-to-noise ratio) and subtraction of the spectral background are necessitated in the measurement of the spectra. The characteristics of the SIT-OMA system mentioned above are suitable for this purpose and have been utilized in the present work to study the molecular fluorescence of PO in various analytical flames.

Experimental

The experimental components used in the present studies are listed in Table VIII, along with the appropriate manufacturers, and a block diagram of the experimental system is shown in Figure 14. An Eimac 150 W xenon arc lamp having a diameter of 25 mm was focused at the center of the flame above the burner top by a lens. Although a different model, the dc power supply for the Eimac lamp was similar to those described earlier. The monochromator wavelength control was calibrated by correlation of readings from the wave-length dial with the atomic lines emitted by a mercury pen lamp. A Perkin-Elmer burner/nebulizer assembly was used, with modification of the burner head as described previously. Two kinds of capillary burner heads were used: one with large diameter capillaries was used for the air-acetylene and air-hydrogen flames, and one with smaller diameter capillaries was utilized for the nitrous oxide-acetylene and oxygen/argon-hydrogen flames.

Table VIII

Experimental Components and Manufacturers of Equipment Used in Flame Molecular Fluorescence Spectrometer System

Item	Model Number	Manufacturer
CW Source		
Arc Illuminator	X6163R	Eimac Div. of Varian, San Carlos, Ca 94070
Power Supply	P-250S-2	Eimac Div. of Varian, San Carlos, Ca 94070
Monochromator	EU-700	GCA/McPherson, Acton, Ma 01720
Detector		
SIT	1205D	Princeton Applied Research Corp., Princeton, NJ 08540
OMA	1205A	Princeton Applied Research Corp., Princeton, NJ 08540
Recorder	715M	MFE Corporation, Salem, NH 03079
Burner/Nebulizer	303-0110	Perkin Elmer, Norwalk, Ct 06852

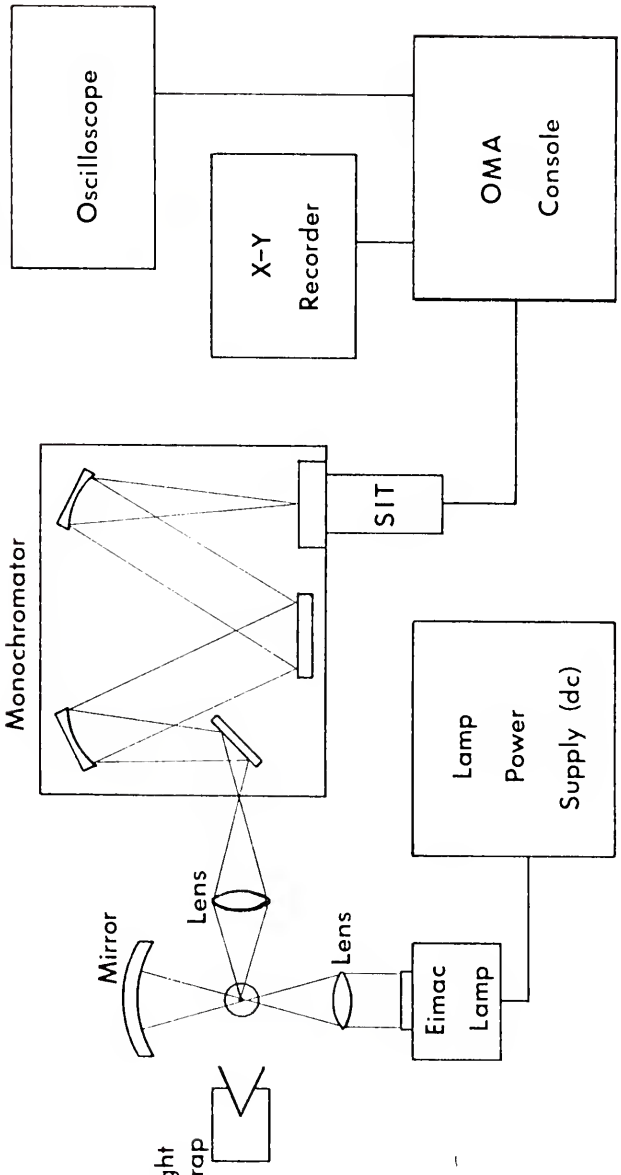


Figure 14. Schematic diagram of the SIT-OMA system as utilized in the present study.

All flame conditions employed are summarized in Table IX. The height of the optical plane was 2.5 cm above the burner top in all cases. In the air-hydrogen and oxygen/argon-hydrogen flames, including their argon separated counterparts, an inner cone of unevaporated solvent droplets was observed which extended from 1 to 3 cm above the burner head. The droplet zone scattered radiation from the excitation source and resulted in a large scattering background signal. Therefore, observation heights lower than ≈ 2 cm were not used for measurements of PO fluorescence spectra in this study. Measurements of the fluorescence signal were taken as a function of the height of the optical plane above the burner head, and the signal was found to decrease as the height was increased above the tip of the inner cone of solvent droplets.

The SIT detector used in the present study contained a plastic scintillator fitted onto its faceplate; this was a required accessory for observations in the UV because of the poor transmission characteristics below 350 nm of the fiber-optic faceplate of the intensifier. The detector was mounted at the exit port of a 0.35 m, f/6.8 Czerny-Turner monochromator which was modified to accept the detector housing.

The OMA employed for this work was equipped with "delay" and "preset" controls for regulation of the number of machine cycles (scans of either the data or background

Table IX

Flame Types and Conditions

Flame Type[a]	Gaseous Flow Rate (ℓ/min)						
	Air	C_2H_2	N_2O	H_2	O_2	Ar	Ar (Separation)
N_2O-C_2H_2		4.5	11				--
Ar-N_2O-C_2H_2		4.5	11				15
Air-C_2H_2	14	2.75					--
Ar-Air-C_2H_2	14	2.75					15
Air-H_2	13			10			--
Ar-Air-H_2	13			10			8
O_2/Ar-H_2				10	2.6	13	--
Ar-O_2/Ar-H_2				10	2.6	13	8

[a] Ar- means Ar separated flame.

channels), and therefore, the integration time, applied to any given analytical determination. The "delay" control established the number of machine cycles to be counted as a single data point in the OMA memory circuits, while the "preset" control fixed the total number of data points to be integrated in each spectral channel of the OMA.

Emission and fluorescence signals were observed simultaneously by the present SIT-OMA system, and thus the signals obtained were not purely fluorescence but rather fluorescence enhanced by emission. However, fluorescence spectra were produced by electronically subtracting the emission from the fluorescence-plus-emission spectra, utilizing for this purpose the two data storage (memory) banks of the OMA. Emission was collected in one memory bank by recording the spectrum with the excitation source shut off, and fluorescence-plus-emission was collected in the other memory bank by recording the spectrum with the excitation source turned on.

The target of the image detector in the present system had 500 vertically oriented spectral channels for the data (or background) arranged in a horizontal row in the focal plane of the monochromator so as to intercept a portion of the linearly dispersed spectrum which appeared at the exit port of the monochromator. The 500 channels covered almost 50 nm of the spectrum, which was wavelength-calibrated by observing the atomic fluorescence spectrum of a

mixture solution of Cd, Ni, Co, Fe, and Pt. In almost all cases, 2000 machine cycles of SIT, which corresponded to a "delay" of 3 and a "preset" of 500 on the OMA, were chosen for the measurements of molecular fluorescence spectra. The time for one machine cycle (one scan of the data or background channels) was 32.8 ms; hence, the system required 65.6 s for one fluorescence spectrum. Longer accumulation times resulted in fluorescence signals which exceeded the memory dynamic range (10^5) of the OMA, and shorter accumulation times were not sufficient to obtain a good signal-to-noise ratio. All spectra were recorded with an X-Y recorder connected to the X and Y plotting outputs of the OMA.

All phosphoric acid (85%, sp. gr. 1.7) used was of guaranteed reagent grade. Deionized water was used as the reference for the background.

Results and Discussion

Molecular bands of PO have been thoroughly investigated in vacuum discharge tubes and in flames by both emission and absorption spectroscopy (27,40,42,45), but not by fluorescence spectroscopy. It is known that PO shows three band systems: a continuum band system near 540 nm a β-system near 324 nm and a γ-system near 246 nm (27). As previously discussed, the β-system and the γ-system are caused by the transitions $B^2\Sigma\ X^2\Pi$ and $A^2\Sigma$-$\chi^2\Pi$, respectively,

where $B^2\Sigma$ and $A^2\Sigma$ are the excited electronic energy states and $X^2\Pi$ is the ground state of the PO molecule.

Molecular fluorescence spectra were measured in the UV for each of the flames listed in Table IX; aqueous solutions of phosphoric acid were nebulized into these flames to obtain fluorescence. Fluorescence spectra observed in the air-hydrogen flame and in the argon separated air-hydrogen flame are shown in Figure 15. As can be seen in these spectra, peak fluorescence signals were observed near 230, 238, 254, and 262 nm. The intensities of the molecular fluorescence signals were higher in the argon separated air-hydrogen flame than in the unseparated air-hydrogen flame. Further, the argon separated flame produced less background noise than the unseparated flame.

The β-system of PO near 324 nm was also examined in the air-hydrogen flame. The β-system bands were very weak, i.e., less than 600 counts per 2000 machine cycles at the wavelength of highest intensity (for a 1 M H_3PO_4 solution and an 850 μm slit width) as compared with ~10^4 counts for the γ-system; moreover, the observed signals were largely emission rather than fluorescence.

In order to compare molecular fluorescence signals in various flames, the fluorescence signals were measured in each of the flames listed in Table X. The results indicate that the signals observed in the air-hydrogen, the air-acetylene, the oxygen/argon-acetylene, and the corresponding

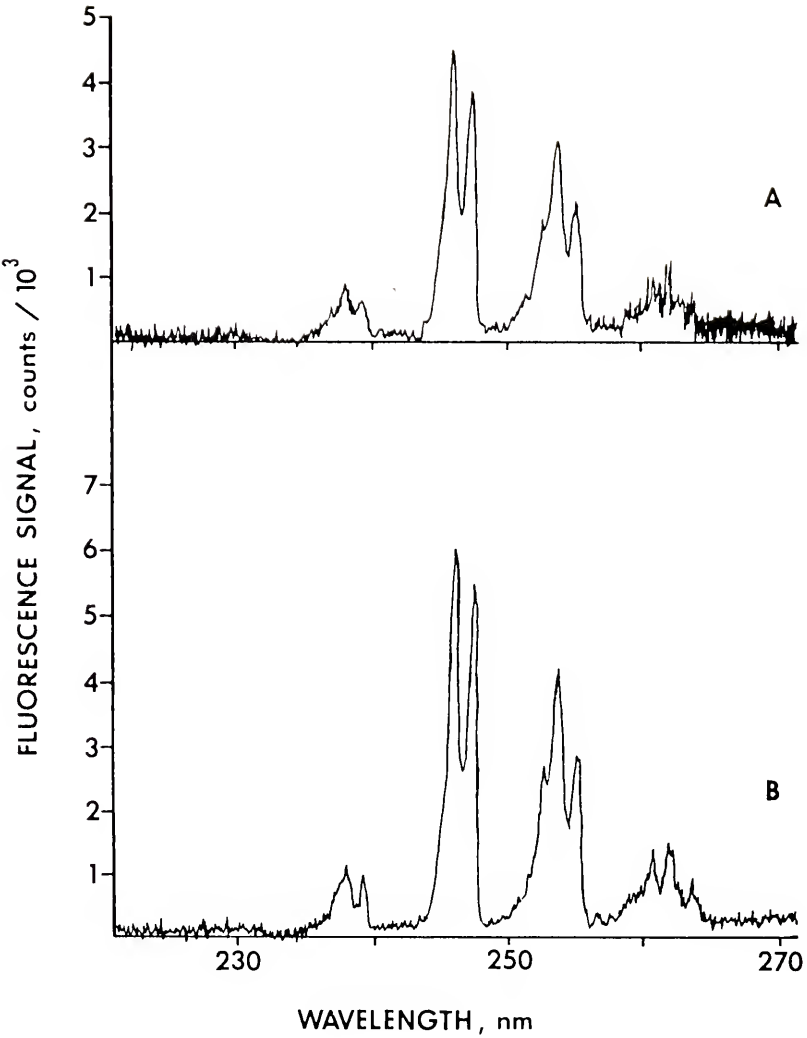


Figure 15. Molecular fluorescence spectra of PO in (A) the air-hydrogen flame and (B) the argon separated air-hydrogen flame, resulting from the aspiration of a 1 M H_3PO_4 solution into the flames. Experimental conditions: slit width = 100 μm; OMA "delay" = 3; OMA "preset" = 500.

Table X

Comparison of the Fluorescence Intensities of PO in Various Flames

Flame Type[a]	Fluorescence Intensity (counts)[b]	
	100 μm[c]	850 μm[c]
N_2O-C_2H_2	9680 (31050)[d]	--
Ar-N_2O-C_2H_2	9450 (29040)[d] (5250)[e]	--
Air-C_2H_2	6760	--
Ar-Air-C_2H_2	6550 (1800)[e]	41,070 (11020)[e]
Air-H_2	4540	--
Ar-Air-H_2	6680	36,550
O_2/Ar-H_2	1100	--
Ar-O_2/Ar-H_2	2200	13,610

[a] Ar- means the Ar separated flame.

[b] Counts per 2000 machine cycles (delay 3, preset 500), at 246 nm, produced by a 1 $\underline{M}$ H_3PO_4 solution.

[c] Monochromator entrance slit width.

[d] Total signals, i.e., fluorescence enhanced by emission.

[e] Fluorescence signals due to the PH_3 concomitant in acetylene, which were measured while aspirating only water into the flames.

argon separated flames are due almost entirely to molecular fluorescence, while the signals from the nitrous oxide-acetylene and argon separated nitrous oxide-acetylene flames are due to fluorescence enhanced by emission. The spectra observed with the argon separated nitrous oxide-acetylene flame are shown in Figure 16. The fluorescence spectrum of Figure 16A was obtained by the subtraction procedure described earlier. As can be seen in Figure 16, the fluorescence signal was about 30% of the total signal in the nitrous oxide-acetylene flame. The fluorescence signals were observed to decrease in the following order of the flames: N_2O-C_2H_2 > Ar-N_2O-C_2H_2 > air-C_2H_2 > Ar-air-H_2 > Ar-air-C_2H_2 > air-H_2 > Ar-Ar/O_2-H_2 > Ar/O_2-H_2, where Ar- means the argon separated flame, and Ar/O_2 indicates the mixture of approximately 80% argon and 20% oxygen which was substituted for air.

As has been reported previously (42,45), phosphate ion is decomposed partially into phosphorus atoms and PO molecules in the nitrous oxide-acetylene flame, while PO_x ($x \geq 2$) molecules are responsible for the primary absorption bands in the air-acetylene flame (45). Taking account of these facts along with the results of this work, the total population of PO appears to be largest in the nitrous oxide-acetylene flame. In the low-temperature flames of the air-hydrogen and argon/oxygen-hydrogen mixtures, the corresponding argon separated flames gave higher fluorescence

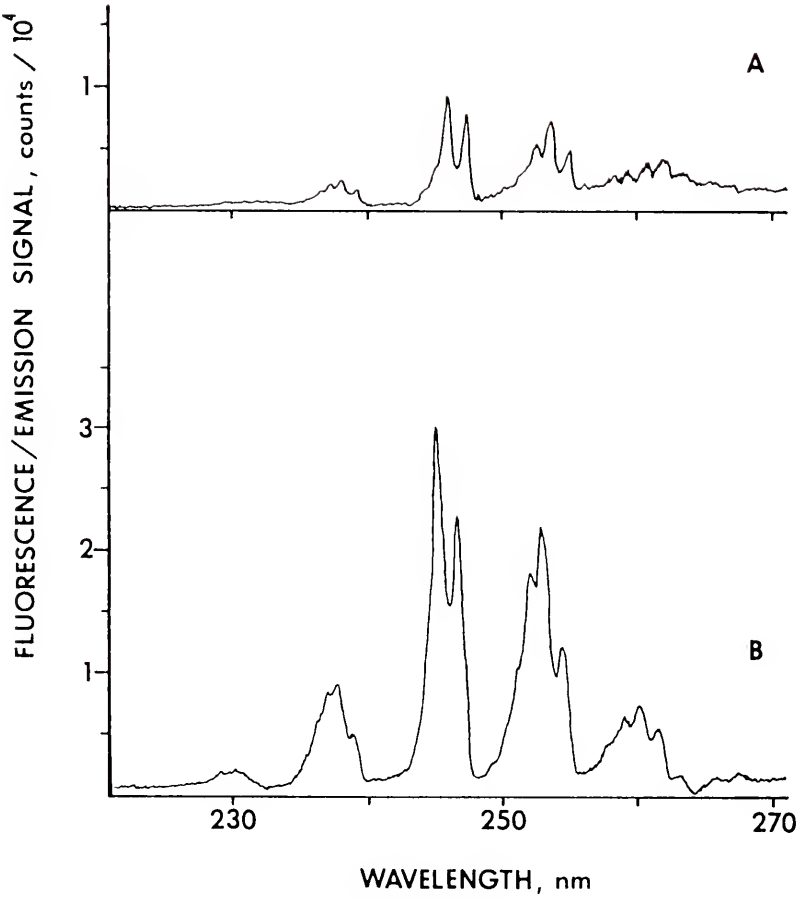


Figure 16. The pure fluorescence (A) and fluorescence enhanced by emission (B) of PO in the argon separated nitrous oxide-acetylene flame, obtained from a 1 M H_3PO_4 solution aspirated into the flame. Experimental conditions are as listed for Figure 15.

intensities than their unseparated counterparts. This may be explained as follows: in the unseparated flames, the recombination of PO with excess oxygen in the entrained air occurs in the flame, decreasing the population of PO.

The intensity of fluorescence depends upon quenching effects of the co-existing flame gases, and nitrogen gas is known to have a large quenching cross section (10). Therefore, in order to examine the quenching effect of nitrogen gas on the PO fluorescence, the fluorescence signals of PO were compared in the air-hydrogen and the argon/oxygen-hydrogen flames, where the Ar/O_2 ratio was approximately the same as that of N_2/O_2 in air. Contrary to expectations, the air-hydrogen flame, which contains nitrogen gas, produced higher PO fluorescence intensities than the argon/oxygen-hydrogen flame (see Table X). This suggests that the fluorescence of PO depends in a complicated manner upon the flame temperature and the quenching effects of flame gases. However, this experiment was duplicated on another system using acetylene as the fuel gas, and a slightly enhanced signal was observed for the nitrogen-free flame, i.e., the reverse situation was observed. The need for more work in this area is indicated.

In order to utilize the fluorescence of PO for the analysis of phosphorus, the signal-to-noise ratio, precision, and limit of detection have been determined for phosphoric acid nebulized into the various flames. As can be seen in

Figure 15, the argon separated flames yielded lower noise levels, by a factor of 2 or 3, than their unseparated counterparts. It should be pointed out that the dominant source of noise in the SIT-OMA system was the flame rather than the detector. The experimental results indicated that the argon separated air-hydrogen flame produced the best signal-to-noise ratio and limit of detection.

As mentioned above, the nitrous oxide-acetylene and air-acetylene flames produced higher fluorescence intensities than other flames, but the background flame noises (and PO fluorescence due to PH_3 in acetylene) were still present and hence the signal-to-noise ratios associated with these flames were lower. In the present work, phosphine in acetylene resulted in a fluorescence signal equal to about 25% of that for a 1 M H_3PO_4 solution aspirated into the air-acetylene flame (see Table X).

The dependence of the fluorescence intensity of PO on the slit width of the monochromator is shown in Figure 17, and fluorescence spectra of PO recorded while employing an 850 μm slit width (Part A) and a 100 μm slit width (Part B) are shown in Figure 18. As can be seen in the spectra of Figure 18, the fine structure of the PO band was lost when the 850 μm slit was used, but the band intensity was greatly enhanced. The plot of fluorescence signal versus slit width (Figure 17) reached essentially a plateau for slit widths greater than 750 μm. The limit of

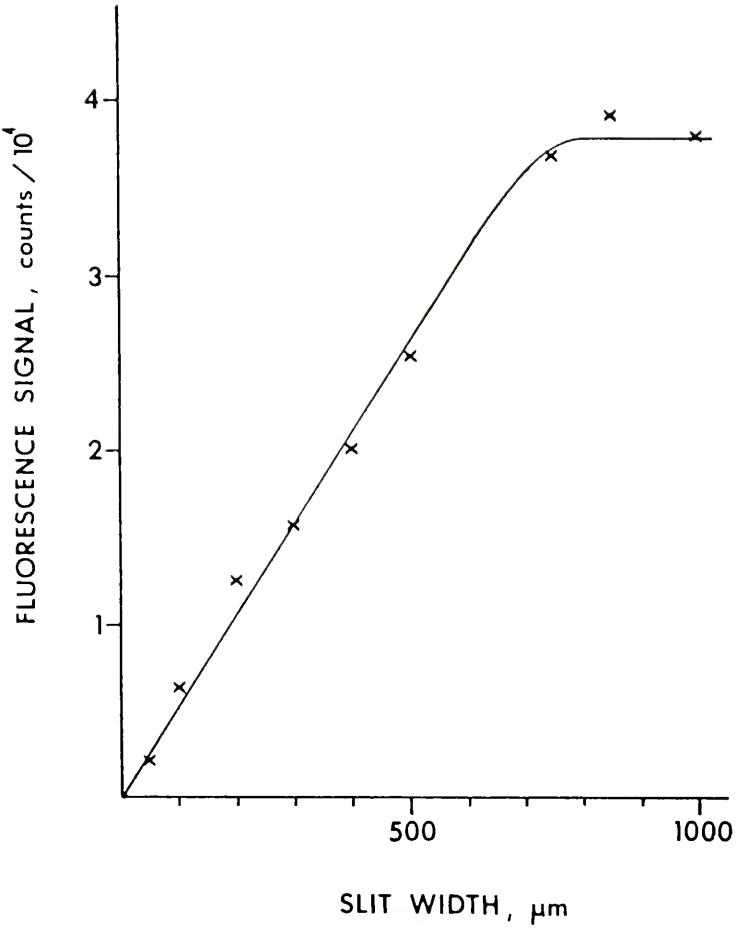


Figure 17. Fluorescence intensity of PO vs monochromator entrance slit width for an argon separated air-hydrogen flame. Solution and experimental conditions are as listed for Figure 15.

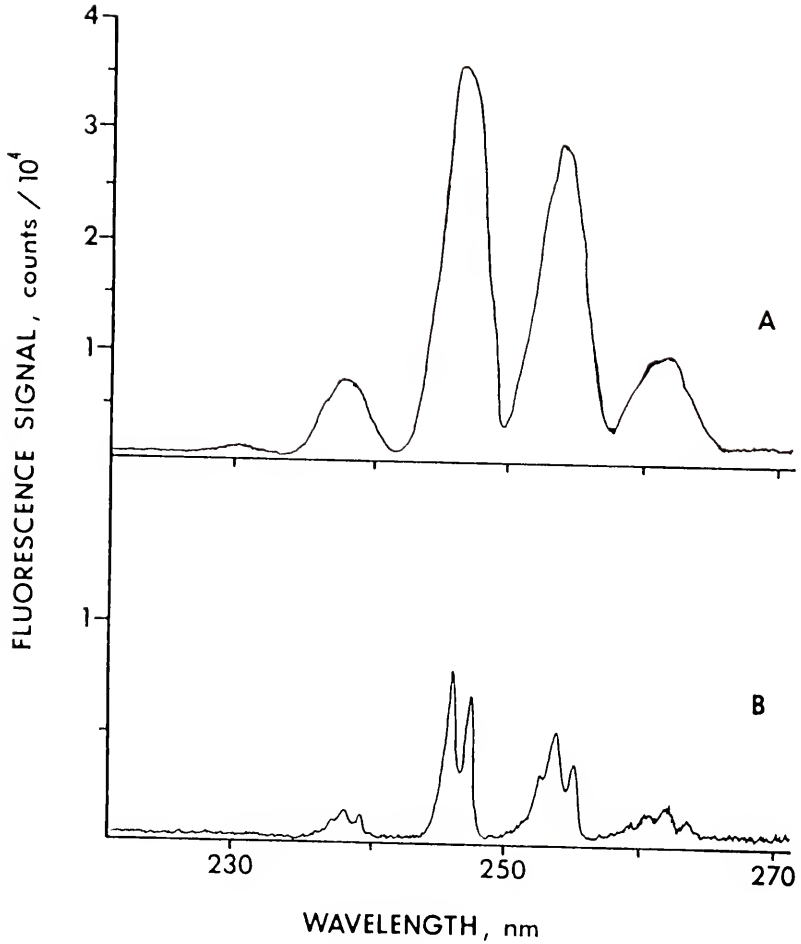


Figure 18. PO fluorescence spectra in the argon separated air-hydrogen flame. Slit widths of 850 μm (A) and 100 μm (B) were used.

detection for phosphorus was about 80 μg P/ml (for a signal-to-noise ratio of 2), and the precision was better than 5% RSD for a 0.5 M H_3PO_4 solution. The analytical curve for PO fluorescence versus phosphoric acid concentration was linear from 0.01 M to 1 M H_3PO_4. Therefore, self-absorption processes for PO in the flame did not appear to be important even at very high phosphorus concentrations.

The ability of the SIT-OMA system to discriminate against noise appears to be significantly inferior when compared with the more conventional signal processing and detection systems used in the studies of the previous chapters. This conclusion is in general agreement with most of the other published evaluations of the SIT-OMA system.

CHAPTER V

CONCLUSIONS AND DIRECTIONS FOR FUTURE RESEARCH

The pulsed Eimac xenon arc continuum source presently offers little improvement as a source of excitation in atomic fluorescence spectrometry over the same lamp operated in the cw mode. A lamp especially suited to pulsed operation is needed, along with a way to reduce or eliminate the particularly severe background interference from molecular fluorescence (and scatter) associated with the operation of the pulsed continuum source, such as removal of the interfering species from the flame, if possible, and/or manipulation of flame conditions.

Flame background molecular fluorescence has been shown to represent a potentially serious form of interference in atomic fluorescence spectrometry with a continuum source, and along with improvements in source intensities and signal-to-noise ratios these interferences should become more prominent, more numerous and, therefore, more troublesome. The types of studies initiated here will have to be extended to other flames and to different observation heights in the flames to see if there is a way to experimentally minimize this problem. A mathematical expression giving the total deteriorative effect of the absorption,

emission, and fluorescence of a molecular band upon the observed atomic fluorescence signal-to-noise ratio should prove to be of considerable value in assessing the extent of interference from molecular species in practical analytical work.

The possibility of direct spectral interferences from fluorescing molecular species introduced into the flame by aspiration of the sample is also a serious concern. Extensive tests of various commonly occurring sample matrices (e.g., blood plasma, engine oils, dissolved vegetable matter, dissolved mineral ores, etc.) will be necessary to provide some idea of the potential severity of this problem.

The question of possible utilization of flame molecular fluorescence for the analysis of non-metallic elements and compounds has only just begun to receive attention from analytical chemists. Because molecular bands are fairly broad in comparison to atomic lines, the application of a sensitive spectrometer with a broad spectral bandpass and good noise discrimination characteristics should enable researchers to effectively evaluate this possibility for a wide variety of non-metallic elements and compounds. Also, the potential for application of non-resonance molecular fluorescence (using a broad-band excitation monochromator or broad-band tunable dye-laser) to this area of research offers considerable promise for improvements in sensitivity.

Finally, the fluorescence of molecules in flames will have to undergo an extensive characterization from a more fundamental point of view. The attempts described here to study the quenching effect of nitrogen were inconclusive because different results were obtained in separate experiments. Human and Zeegers (35) found molecular fluorescence quantum efficiencies to be comparable in magnitude to efficiencies reported for atoms but were unable to interpret their findings with regard to the yet unexplained fine structure of the molecular fluorescence bands. They also learned that absorbed radiant energy underwent extensive re-distribution among the various vibrational and rotational energy levels before being re-radiated as fluorescence. These types of studies will have to be repeated and extended in order to learn more about flame molecular fluorescence and fundamental flame processes.

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BIOGRAPHICAL SKETCH

William Kelly Fowler was born in Lexington, Kentucky on September 10, 1948. He attended public schools in Owensboro, Kentucky until graduation from high school in June, 1966. After graduation from Centre College of Kentucky with a Bachelor of Arts degree in Chemistry (1970), he taught chemistry, physics, and physical science in high school for one year. In 1971, he entered the University of Florida as a graduate student in the Department of Chemistry, College of Arts and Sciences. In addition to his teaching experience, he has spent several summers employed in either laboratory or research assistant capacities.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Assistant Professor of Chemistry

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1976

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